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The report reviews current understanding of man-made causes of changes in stratospheric ozone including releases of chloroflurocarbons (CFCs), nitrous oxide, nitrogen oxides, methane, carbon dioxide, and other trace gases. Results of up-to-date models are prescuted. The report also reviews current understanding of the biological consequences of changes in stratospheric ozone, focusing on effects of increased exposure to solar ultraviolet-B radiation that would accompany decreases in ozone.

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Preface

This report describes the findings of recent research and the resulting improvements in scientific understanding of the causes and effects of changes in stratospheric ozone. The report is one in a series on the subject prepared under the auspices of the National Research Council. Our purpose has been to update the information contained in the most recent NRC report in the series, Causes and Effects of Stratospheric Ozone Reduction: An Update (1982).

The report was prepared at the request of the U.S. Environmental Protection Agency. Under the provisions of the Clean Air Act as amended (Title I, Part B: 42 USC 7450 et seq.), the agency is required to report to Congress biennially on the status of research related to protection of stratospheric ozone.

The report is divided into two parts: Part I deals with changes in the atmosphere and perturbations to stratospheric ozone, Part II with effects of changes in ultraviolet-B (UV-B) radiation that would accompany changes in the total amount of ozone above the Earth's surface. Each part contains its own introduction and summary and its own citations to the scientific literature. The subjects of the two parts are treated separately because they involve different types of scientific expertise and are linked only by their relationships to the intensity and spectral distribution of ultraviolet light at the Earth's surface. Taken together, however, the two subjects define the state of knowledge needed to carry out the provisions of the Clean Air Act.

It should be noted that potential changes in stratospheric ozone are not the only influences leading to increased exposure of humans to ultraviolet-B

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radiation. As described in Part II, certain social, recreational, and economic trends are leading to increased exposure. Consequently, the analyses provided in Part II have implications beyond the context of protection of stratospheric ozone. Similarly, changes in atmospheric ozone may have consequences other than those associated with UV-B.

In conducting its study and preparing this report, the Committee was assisted by a number of NRC staff members, among them Myron F. Uman, Kate Nesbet, Roseanne Price, Estelle Miller, and Robert Rooney. I express my appreciation for their effort and for the selfless dedication of my colleagues on the Committee.

Leonard C. Harber
Chairman

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PART I

Perturbations to Stratospheric Ozone

1

Introduction and Summary

Ozone, the triatomic molecule of oxygen (chemical formula O_3), absorbs short-wavelength ultraviolet (UV) solar radiation that can be harmful to animal and plant life (NRC 1973, 1975, 1976b, 1982). Ozone is present in the upper atmosphere in small amounts and prevents most of this radiation from reaching the Earth's surface. If all of the ozone in the atmosphere was distributed uniformly over the surface of the Earth at sea level, it would form a layer only about 3 millimeters (mm) thick. Most of the atmospheric ozone (roughly 95 percent) is found in the stratosphere, a layer of the atmosphere at altitudes from about 16 kilometers (km) to 50 km at low latitudes and about 8 to 50 km at high latitudes. The lower and upper limits in altitude are called the tropopause and the stratopause, respectively, and represent minima and maxima in atmospheric temperature. The rise in temperature with altitude in the stratosphere is a consequence of the absorption of ultraviolet radiation by ozone and its conversion into heat. This inverted thermal structure in turn inhibits vertical transport. Ozone is a highly reactive chemical. Near ground level, the relatively high concentrations of ozone that may occur from time to time during air pollution episodes over parts of North America are harmful to public health and welfare (NRC 1977, U.S. EPA 1978).

The concentration of stratospheric ozone is maintained by a balance of processes that create and remove it (Figure 1-1). Ozone is created in a photochemical process that begins with the photolysis of diatomic oxygen (O_2). It is destroyed in several complex series of chemical reactions involving oxygen (O), hydrogen (H), chlorine (Cl), and nitrogen (N) compounds, with the last three acting as catalysts at very small concentrations.

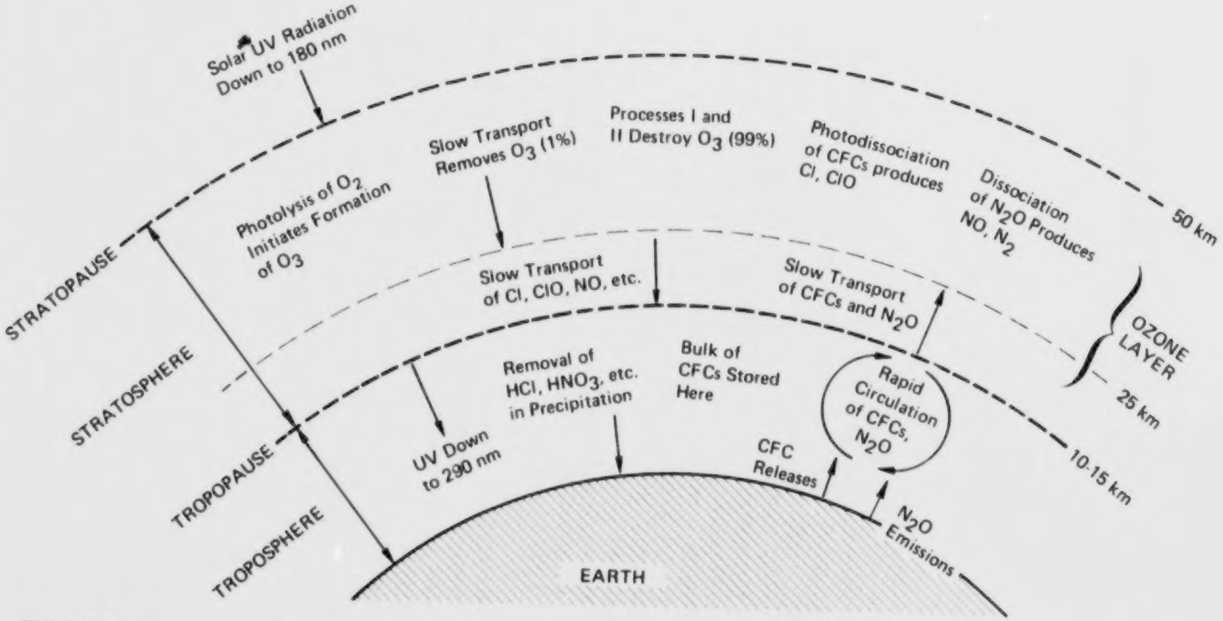
Solar UV Radiation
Down to 180 nm
STRATOPAUSE
STRATOSPHERE
TROPOPAUSE
TROPOSPHERE
Photolysis of O2 Initiates Formation of O3
Slow Transport Removes O3 (1%)
Processes I and II Destroy O3 (99%)
Photodissociation of CFCs produces Cl, ClO
Dissociation of N2O Produces NO, N2
50 km
Slow Transport of Cl, ClO, NO, etc.
Slow Transport of CFCs and N2O
OZONE LAYER
25 km
Removal of HCl, HNO3, etc. in Precipitation
Bulk of CFCs Stored Here
Rapid Circulation of CFCs, N2O
10-15 km
UV Down to 290 nm
CFC Releases
N2O Emissions
EARTH

FIGURE 1-1 Representation of the processes that determine the concentration of ozone in the stratosphere. SOURCE: NRC (1982).

Ozone is also removed from the stratosphere by large-scale transport processes. For descriptions of the chemical and dynamic processes and a sequence of assessments of understanding about them, see NRC (1975, 1976a, 1979, 1982), NASA (1979a), WMO (1982a), and Bower and Ward (1982).

In the early 1970s it was realized that human activities result in the addition of certain chlorine, nitrogen, and other catalyst species to the stratosphere, upsetting the balance between production and destruction processes and leading to changes in the total amounts of ozone above the Earth's surface. Among the chemical agents considered to have the potential to affect stratospheric ozone in various ways are nitrogen oxides (NO_x), chlorofluorocarbons (CFCs), nitrous oxide (N_2O), methyl chloroform (CH_3CCl_3), carbon tetrachloride (CCl_4), methane (CH_4), and carbon dioxide (CO_2). Among the CFCs the most important are CFC-11 ($CFCl_3$) and CFC-12 (CF_2Cl_2). A reduction in stratospheric ozone would lead to an increase in the intensities of UV light reaching the Earth's surface, and the consequences would potentially be harmful (see Part II of this report).

The oxides of nitrogen (NO_x) are the major chemical family responsible for the loss of ozone in the stratosphere. The addition of significant quantities of NO_x to the stratosphere--for example, from increasing concentrations of N_2O, detonation of nuclear weapons, or substantial numbers of supersonic aircraft--would result in substantial decreases in the total amount of ozone. A small increase in atmospheric N_2O (of 0.2 percent per year) has been observed and is taken into account in current scenarios. Current models do not account for emissions of NO_x from commercial fleets of supersonic aircraft, however, mainly because there are no plans for such fleets currently under consideration. If, however, we were to envision a fleet of such aircraft similar to that of CIAP (1975), the most recent chemical models would yield substantial ozone depletions (in the range of 8 percent or more). Most of the projected increases in atmospheric NO_x are assumed at present to be injected into the upper troposphere by subsonic commercial aircraft. Contrary to the case of the stratosphere, the addition of NO_x to this region of the atmosphere leads to production of ozone, which is further enhanced by global increases in concentrations of methane and other hydrocarbons. Excess tropospheric NO_x may produce substantial increases in the local concentration of ozone in the troposphere and modest increases in the total amount of ozone in the atmosphere.

This report focuses on the effects of additions of chlorine to the stratosphere due to releases of CFCs and other halocarbons. It also takes account of changing concentrations of other trace gases, such as CO_2, CH_4, and N_2O, which may be the result of human activities and/or natural processes. It is clear that, over the past century or more, human activities have led directly or indirectly to changes in the chemical composition of the atmosphere. Stratospheric concentrations of chlorine are now more than twice the value associated with natural sources (methyl chloride [CH_3Cl]). This change can cause substantial perturbations to the chemical reactions controlling the abundance of ozone in the stratosphere. We do not emphasize anthropogenic additions of NO_x to the stratosphere because current estimates of future emissions to the stratosphere do not include substantial injections of this pollutant.

Observing the changes in the chemistry of the stratosphere due to the release of trace gases is difficult. The substances of interest are present in only trace amounts, and many of them are difficult to measure. The approach to the problem has been to develop theoretical descriptions, or models, of the physical and chemical processes thought to be important in the stratosphere. These models are used to calculate the concentrations of various species as a function of position and time. To validate the models, calculations are compared with observational data. Laboratory experiments are performed to obtain photochemical rate coefficients that are used in the models. As our understanding of stratospheric processes increases, we may use the models to estimate the consequences of releases of trace gases for changes in stratospheric ozone in the future.

In Part I of the report, we present an update of earlier reviews of our understanding of the changes in stratospheric ozone that may be caused by human activities. The emphasis is on results of research performed in the last two or three years. In particular, we examine the most recent advances in laboratory measurements (Chapter 2), field observations (Chapter 3), understanding of dynamic meteorological processes (Chapter 4), comparisons between model calculations and measurements (Chapter 5), and estimates of the consequences of continued chemical perturbations for the future (Chapter 6). Below is a summary of the chapters, followed by a brief discussion of uncertainties and conclusions. Recommendations for future research are included in each chapter.

SUMMARY

Laboratory Measurements

As a result of recent laboratory studies, the rate parameters for many photochemical reactions have been revised. These reactions involve radicals and unstable chemical species that pose formidable experimental problems. The new studies, using significantly improved measurement techniques, have reduced uncertainties in the data. As indicated in Chapter 6, most of the revisions have led to estimates of smaller ozone reductions because of man-made perturbations. A few examples are given in Chapter 2.

For example, recent laboratory studies have quantitatively demonstrated the formation of chlorine nitrate ($ClONO_2$) in the reaction of chlorine monoxide (ClO) and nitrogen dioxide (NO_2), favoring $ClONO_2$ as a principal product channel rather than other isomeric species with unknown structures and reaction rates. The results reduce a major uncertainty in modeling the interaction of chlorine and nitrogen species in the stratosphere.

Measurements of the flux of solar radiation in the range of wavelengths critical to photochemical production of ozone in the stratosphere (from 187 nanometers [nm] to 225 nm) have led to values for the O_2 absorption coefficients that are 25 to 50 percent smaller than earlier laboratory values. The revision of the cross sections to lower values appears to have been confirmed by a recent laboratory study. The O_2 absorption coefficients determine the depth to which radiation in this wavelength interval penetrates the stratosphere and, in so doing, determine the rate at which ozone is produced in the stratosphere. Accordingly, the new data have caused substantial revisions in the results of photochemical models and have lowered our estimates of the extent of total ozone perturbations caused by human activities.

Field Measurements

Different types of instruments that measure the same trace species in the atmosphere are now being compared simultaneously under field conditions. Rigorous, double-blind comparisons provide an assessment of the reliability with which the abundance of key stratospheric species can be measured and, as a result of discovered differences, stimulate the refinement of experimental techniques. For example, the findings of balloon-borne instruments for measuring both stratospheric ozone and water vapor have recently been compared in separate multiple-balloon campaigns. The ozone study revealed the need to examine more closely the reliability of most ozone instruments for measurements at altitudes above 40 km. The water vapor study indicated that stratospheric water vapor can probably be measured with reasonable accuracy (to within ±1.5 parts per million by volume [ppm]), but unexplained systematic differences contribute substantially to the current uncertainty.

Several sets of data on trace constituents, in addition to ozone, obtained from satellites (Stratosphere and Mesosphere Sounder [SAMS], Limb Infrared Monitor of the Stratosphere [LIMS], and Solar Mesosphere Explorer [SME]), have been reviewed and are now available. The global and nearly continuous coverage obtained with satellites provides considerable insight into large-scale chemical phenomena. The SME and LIMS measurements have confirmed that the abrupt decrease of stratospheric NO_2 at about 45°N in the winter is indeed a polarwide phenomenon associated with the edge of the polar vortex. The SAMS measurements of CH_4 and N_2O have confirmed the general features found in the altitude profiles obtained with balloons and aircraft and, by virtue of the extensive coverage, have revealed features in the global distribution of these long-lived gases. Lastly, information about the abundance of species that are not directly measured by satellite can be inferred from the data. Ratios of the LIMS data on NO_2 and nitric acid (HNO_3) yield preliminary estimates of the hydroxy radical (OH) in the middle stratosphere that are consistent with the limited number of previous direct measurements.

A new balloon-borne technology promises to provide more reliable determination of vertical profiles. An instrument platform has been suspended beneath a balloon floating at its maximum altitude, and has been let down and reeled up over a distance of 12 km. Repeated observations within a short time span should give a measure of the natural, short-term variability as well as resolving the diurnal behavior of the profiles for comparison with model calculations.

Meteorological Processes

Analyses of meteorological data on the stratosphere from satellite data accumulated over more than 10 years have revealed unexpectedly large year-to-year variability in the winds and temperatures. Substantial interannual variability also occurs in the distribution and amount of stratospheric ozone. This large year-to-year variability makes it impossible to derive definitive ozone trends from short-term records, and indicates the additional complexity associated with atmospheric transport processes.

The mechanics of the exchange of trace species between the troposphere and the stratosphere have received renewed attention in the past few years. Recent observations from aircraft in the equatorial regions suggest that traditional ideas about the transport of water vapor and other tropospheric species into the stratosphere may need modification. The exchange of water vapor between the troposphere and stratosphere now appears to have strong longitudinal and seasonal dependence and to be associated with small-scale dynamical processes occurring in convective clouds.

Meteorological processes are also coupled to ozone perturbations through the radiative effects of ozone and other trace species. Tropospheric species that may produce significant photochemical perturbations of ozone (e.g., CFCs, CH_4, N_2O) may, through absorption of infrared radiation, contribute to the atmospheric greenhouse effect. Recent estimates indicate that if current trends in the concentrations of these minor gases continue, their direct radiative effects may produce a warming at the surface comparable to that attributed to the projected increase in carbon dioxide. Occurring at the same time, radiative cooling in the stratosphere would influence ozone photochemistry by reducing the rates for many reactions that destroy ozone. Thus, the question of chemical perturbations to ozone may not be considered independently of the climatic alterations due to trace gases such as carbon dioxide.

Comparison of Models and Measurements

The capabilities of theoretical models have continued to grow over the past two years. Most notably, the chemical models have kept expanding to include more sophisticated treatments of dynamical transport and redistribution of trace gases in more than one dimension. These more realistic models are needed for the interpretation of observed data in the proper context of the time and location of the observations.

The reduction in the previously established cross section for molecular oxygen in the Herzberg continuum has led to a significant revision in most photochemical models. Additionally, the kinetic rate coefficients for several important chemical reactions have been revised substantially. In most cases the revisions have led to better agreement between models and observations, while in some cases they have led to larger disparities. Overall, our ability to model the observations of CFCs, N_2O, ClO, NO_3, and OH has improved, but we still have some difficulties predicting the distribution of CH_4, O_3, and some odd-nitrogen species.

Substantial new sets of observations of CFC-11 and CFC-12 are now available. The measurements indicate that the concentrations of these gases are increasing at a rate that may be described by a photochemical model using estimated releases for CFCs and losses due to stratospheric processes only. The scope of perturbations to the atmosphere has expanded with the confirmation of increasing concentrations of atmospheric N_2O and CH_4, the causes of which may be anthropogenic, natural, or both. In addition, the chemical reactions of the atmosphere are affected by the local temperature, which may be perturbed by increases in the so-called greenhouse gases, most notably CO_2.

Detailed statistical analyses of measurements of total ozone between 1970 and 1980 have indicated no discernible trend in the total column abundance of ozone (the net amount of ozone above a unit area of the Earth's surface). The observations are consistent with more recent photochemical models that take account of simultaneously changing concentrations of CFCs, N_2O, CH_4, CO_2, and NO_x.

As has been the case for a number of years, photochemical models calculate that the largest relative local change in ozone for continued releases of CFCs should occur at an altitude near 40 km. New analyses of observed ozone trends are limited by the reliability of the ground-based Umkehr data, but suggest a decrease in ozone concentration at this altitude over the past decade. The magnitude of the observed decrease, approximately 3 percent, is uncertain, but it is in agreement with current theory. Models suggest that the percentage changes in ozone near 40 km are primarily due to chlorine, produced by the photolysis of CFCs.

Chemical Perturbations

Current estimates of the steady-state reduction of total column ozone attributable to releases of CFC-11 and CFC-12 acting alone (at roughly 1980 rates) center around a value of 3 percent. Using similar release rates and the most recent photochemical parameters, described in Chapter 2, several models yield results that range from 2 percent to 4 percent. This calculated reduction in total ozone is sensitive to the physical and chemical parameters of the model; for example, the range would shift to 3 percent to 5 percent if the older, faster rate coefficient for the chemical reaction of O and ClO were used in the calculations. The calculated net column reduction is the result of a substantial decrease in ozone above 30 km, amounting to about 6 percent of the total quantity of ozone in the atmosphere, and a smaller increase in ozone below 30 km, amounting to about 3 percent of the total ozone. Large local ozone reductions are still calculated to occur near 40 km. These reductions--of up to 60 percent of the local ozone concentration--may be the key to detecting the influence of halocarbons on ozone, and to demonstrating the connection between atmospheric observations, laboratory kinetic measurements, and photochemical models.

The increase in ozone in the lower stratosphere that is calculated for CFC releases suffers from major uncertainties in our modeling of the chemical and dynamical processes and is more difficult to verify. In this region of the stratosphere, dynamical processes maintain strong vertical gradients in the concentration of key trace gases, including ozone. The effect of photochemical reactions on ozone concentrations may be overshadowed by the atmospheric motions that redistribute these gases throughout the stratosphere and into the troposphere. Over the past several years, changes in the chemical kinetic data have not significantly altered the calculated decrease in ozone due to CFCs above 30 km. Significant changes have occurred in calculations for the lower stratosphere, however, and it is conceivable that even the sign of the currently calculated increase below 30 km may be reversed with improvements in our ability to model the coupled chemical and dynamical processes of this region. Accordingly, we must allow for the possibility that modifications in our understanding of this region will occur in the next few years.

The detection of a trend in ozone over the past decade has become more complicated with the recognition that ozone may be perturbed by a number of species introduced into the stratosphere and that responses of stratospheric ozone to additions of chlorine and other trace gases may be nonlinear. Ozone in the stratosphere is actually under the simultaneous influence of a number of compounds of known or suspected anthropogenic origin. Among these are CFC-11, CFC-12, N_2O (each of which can act to reduce ozone), and nitrogen oxides from commercial subsonic aircraft, CH_4, and CO_2 (each of which can increase ozone). If we consider reasonable scenarios of the recent past and potential future, model calculations suggest that the net column ozone change over the next few decades will probably be on the order of +1 percent. However, this very small calculated net change in total ozone may be fortuitous, and we should not infer from it that serious environmental concerns can be abandoned. For example, if CFC emissions were to increase at a rate of 3 percent per year, and if measures were taken to reduce CO_2 and/or aircraft NO_x emissions, the current models suggest that total ozone could decrease substantially, perhaps by as much as 10 percent by 2040. In another example, if CFC emissions were to double and the methane concentration were to remain unchanged, some models would predict a decrease of about 3 percent by the middle of the next century. One recent modeling study suggests that the ozone column is a nonlinear function of changes in the stratospheric chlorine concentration, further complicating the interpretation of the detection of ozone trends.

An important aspect of ozone change, which must be seriously addressed in the future, is the potential redistribution of ozone in the stratosphere. With large ozone reductions calculated in the upper stratosphere and substantial ozone increases calculated in the lower stratosphere and upper troposphere, the heating rates and dynamics of the upper atmosphere may be noticeably altered. Moreover, the increased concentrations of tropospheric ozone and several other trace gases may cause significant warming at the Earth's surface. The issue of climatic change associated with ozone perturbations has yet to be resolved.

DISCUSSION

It is particularly important to consider the uncertainties inherent in the model calculations, current and past.

Unfortunately, the subject has not been addressed in the scientific literature during the past two or three years, although we may consider the history of model calculations as an empirical example of the uncertainty. The best estimate of the steady-state reduction in the total amount of ozone above the Earth due to CFC releases alone, and in the absence of other perturbations, has changed from 16.5 percent (NRC 1979) to about 7 percent (between 5 and 9 percent, NRC 1982) to about 3 percent (between 2 and 4 percent, this report) for equivalent calculations. The principal factor responsible for this sequence of changes has been improved measurements of photochemical rate parameters. These numbers for ozone reduction do not include estimates of uncertainties in the physics and chemistry of the model calculations, and their successive changes in magnitude can be--and often are--misinterpreted.

A first attempt in estimating uncertainties was carried out by the NRC (1976a). The technique used was a combination of sensitivity analysis on certain parameters of the chemical model and subjective estimates of the uncertainties associated with other parameters, including those associated with transport processes. Although the NRC report carefully described the methods used to arrive at the result, which included many subjective estimates, the use of terminology such as "95 percent confidence level," even with all the expressed precautions, led to interpretations of the result as a well-defined statistical uncertainty. The next NRC report on the subject, in 1979, again quoted a 95 percent confidence level and used more detailed analytical techniques, a combination of sensitivity analysis and Monte-Carlo analysis for most of the input variables. Nevertheless, certain subjective estimates of uncertainties were deemed necessary to account for incompleteness in the modeling of atmospheric processes. The authors of the NRC (1982) report judged that this approach was open to misinterpretation.

Some measure of uncertainties associated with current understanding is important, however, to provide a perspective for those who would use these analyses in decision making. We find it difficult to provide such a quantitative measure, both because this issue has not been addressed analytically in the recent scientific literature, and because any description of the uncertainties associated with the incompleteness of one-dimensional (1-D) models must remain subjective. The heart of the issue, given the history of changing estimates in the predicted ozone depletions, is the extent to which we can have confidence that our understanding has improved.

First, the evidence reviewed in this report suggests that the theory of humanly induced chemical change in the stratosphere remains valid. For example, the steady increase in tropospheric concentrations of CFCs (Chapter 5) shows that these compounds are not rapidly removed from the atmosphere. Their vertical distributions clearly indicate that the major destruction process for them is photolysis in the middle and upper stratosphere, leading to the injection of substantial amounts of chlorine at those altitudes. The fast catalytic destruction of ozone by chlorine atoms is also fully established by laboratory experiments, even though some uncertainties remain regarding the precise magnitude of the critical rate coefficients (Chapter 2). Field studies--in particular, comparisons of measurement techniques--have improved our ability to make measurements in the stratosphere and have increased our confidence in the results (Chapter 3). Improved laboratory techniques have resulted in better measurements of a number of important rate parameters (Chapter 2). Using the new rate parameters, we have generally improved agreement between calculations and observations (Chapter 5). It is important to note that all model calculations suggest substantial reductions in ozone in the upper stratosphere (near 40 km) due to continuing injections of chlorine, a result that has not changed substantially over the past decade.

Most of the changes in estimates of steady-state reductions in total ozone during the past four or five years have been the result of a cancellation effect, with reductions in the upper stratosphere and increases in the lower stratosphere and upper troposphere. In the lower stratosphere, dynamical and chemical processes have comparable roles in determining the distributions of trace species. In this region, current models have not been designed to treat both types of processes in comparable detail. Only three-dimensional models, which are yet to be developed, could address this class of questions in detail. Consequently, the uncertainties in current understanding are greatest just where recent models suggest a small percentage increase in ozone that partly balances the relatively larger decrease at higher altitudes.

The range of values given in this report for the steady-state reduction in total column ozone for CFC releases in the absence of other changes reflects more the precision of the art of modeling than the accuracy of the result. Some reduction in the uncertainty of model predictions over the past four years is demonstrated by the general improvement in the agreement between calculated profiles and observations (Chapter 5). However, our estimates of the current uncertainty in chemical models are not substantially different from those of the NRC report of 1979 (16.5 ± 11.5 percent at the 95 percent confidence level), which have been demonstrated to have been overly optimistic. Without further analysis of the sensitivity of model results to changes in input parameters or other features of the models, we will not be able to describe the uncertainties objectively. Research in this area is important. If we were to perform an analysis of uncertainty today of the type described in the NRC report of 1979, we believe that the result, an uncertainty of the order ±10 percent of the total column ozone, would not differ substantially.

A major element of recent research has been the realization that the evolution of the atmosphere is more complex than had earlier been assumed. The chemical composition of the "background" atmosphere is changing continuously (for example, concentrations of both N_2O and CH_4 have been increasing), so that simple calculations assuming a constant atmosphere--except for one perturbation--are of questionable applicability. Models that account for the simultaneous, time-dependent perturbations of a number of species have recently been developed (Chapter 6). These models provide additional insight, but their applicability is also limited because of the questionable reliability of assumptions about trace gases in the atmosphere over time periods of many decades.

Finally, we are encouraged by the continuing advances in atmospheric sciences. Great strides have been made recently in atmospheric measurements of the concentrations of stable and unstable species from balloon-borne platforms and from satellites. These developments will allow more direct and sensitive testing of the models by providing simultaneous measurements of key chemical species as a function of time and altitude and by providing a global picture of trace gases and their variability. Laboratory measurements have become more sophisticated and reliable, improving the accuracy of the chemical and photochemical rate parameters and making abrupt reevaluations less likely in the future.

Two-dimensional calculations have been performed successfully, and the results compare favorably with those of 1-D models, supporting the usefulness of the latter and encouraging further development of multi-dimensional models. All these achievements contribute to enhanced confidence in the theoretical picture of changes in stratospheric ozone induced by human activities.

2

Laboratory Measurements

INTRODUCTION

The preceding, introductory chapter has provided both a general review of the stratospheric ozone problem and a summary of recent findings. Beginning here we examine in greater detail the basic physical problems and recent progress in understanding them: chemical and photochemical transformations (Chapter 2), field measurements (Chapter 3), transport (Chapter 4), and model calculations and their comparisons with measurements (Chapter 5).

It is useful to begin the discussion with an outline of the magnitude of the chemical problem. The most recent evaluation of kinetic and photochemical data by NASA (1982) listed rate constants for 192 chemical reactions and 48 photochemical processes, a total of 240 parameters to be supplied as a result of laboratory studies. While not all of these parameters are needed in the most important model calculations, about half that number, some 100 to 150, are indeed used in most model calculations. Not all, of course, are equally important in affecting the outcome of a given calculation. Although this total number of 200 to 300 parameters includes some processes that occur mainly in the troposphere, a comprehensive description of tropospheric chemistry would involve a very much larger number of reactions.

The chemical rate processes may be subdivided into two-body and three-body reactions, the former being of the general type $A + B \rightarrow C + D$ and the latter of the type $A + B + M \rightarrow AB + M$. Both types are fast processes involving reactive species (atoms, radicals, excited states) whose reactions can affect the chemistry of the stratosphere even at very small concentrations, such as parts per billion by volume (ppb) to parts per trillion by volume (ppt).

Two-body processes may be further subdivided into "direct" and "complex intermediate" reactions depending on whether or not the collision between A and B produces an intermediate, energy-rich structure whose lifetime may be sufficiently long to allow it to be collisionally stabilized. Three-body reactions necessarily involve collisional stabilization of the initial, energy-rich AB molecule by any "third-body" molecule, M, and their rates generally depend both on the nature of M and on its concentration (i.e., on total pressure).

To simulate the large array of chemical reactions affecting stratospheric ozone, we need to know (a) the identity of reactants and products, and (b) the rate constant, k(T), which relates the rate of the process to the concentrations of reactants as a function of temperature. In simple cases, the reaction rate is the product of the rate constant and the concentration of the reactants, $k \times C_A \times C_B$, where C_A and C_B are the concentrations of reactants A and B. We wish to emphasize that laboratory measurement of such rate constants is a difficult matter for several reasons: (1) the desired reactive species must be produced under controlled conditions; (2) they must be brought together with other reactants; (3) their concentrations and/or those of other reactants or products must be measured accurately; and (4) the desired reaction must be isolated as much as possible so as to avoid interference by other processes. In this sense, laboratory studies differ essentially from the atmospheric phenomena to whose understanding they contribute: in the laboratory we attempt to isolate individual, elementary processes, not to recreate the complex conditions that exist in the stratosphere.

The photochemical processes present very different requirements. One needs to know the absorption coefficient of the particular molecule as function of wavelength as well as the quantum yield, i.e., the fraction of absorption events that results in a particular cleavage (photolysis) of the molecule. For polyatomic molecules it is also important to measure the temperature dependence of both the absorption coefficient and quantum yield and to determine the products that are formed.

Direct, reasonably accurate laboratory measurements of radical reaction rates have been made over the past 20 to 25 years. In the last 10 years, the versatility and accuracy of laboratory methods have been greatly improved, largely due to the introduction of laser methods both for radical generation and for detection. Yet, each experimental study brings with it a host of problems resulting ultimately in errors that are difficult to control and that have often been underestimated. In simple, well-controlled reaction systems, experimental precision (repeatability) may be as good as ±3 percent for a given rate constant at a certain temperature. Even then, a realistic estimate of all experimental uncertainties leads to absolute accuracies in the range of 10 to 15 percent. In more complicated systems, 20 percent accuracy may be the best we can expect. Improvement is possible and probable, but is likely to be gradual and less than spectacular because of the complexity of the systems.

If, for example, on the order of 20 reactions are important for the outcome of a certain model calculation, a simple error analysis of the type used in NRC (1979)[1] would predict a total uncertainty of a factor of 2. Yet, the recent history of one-dimensional model calculations of the eventual decrease in ozone due to CFC releases has shown much more drastic changes over the past several years than can be accounted for by small changes in a few rate constants. Why? There are mainly two reasons: (1) for a very few processes, much larger errors had been incurred as a result of circumstances that are easily rationalized in hindsight but not easily predicted; and (2) as had happened before, the large reaction matrix was incomplete and some newly introduced processes produced large effects. The fact that the last three or four such

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[1] The uncertainty in the result of a model calculation (for example, of the reduction R in the total ozone column) is a function of the uncertainties in all of the parameters of the model. A measure of the sensitivity of the output R to changes in one of the parameters (for example, the jth rate constant k_j) is given by $\delta \ln R/\delta \ln k_j$. The expression for this ratio in NRC (1979) contained a typographical error. The correct expression is

$$\frac{\delta \ln R}{\delta \ln k_i} \approx \left(\frac{R - R_o}{R_o}\right) \Bigg/ \left(\frac{k_i - k_o}{k_o}\right) = \left(\frac{R - R_o}{R_o}\right)\left(\frac{k_o}{k_i - k_o}\right)$$

major changes have all resulted in lowering the calculated ozone depletion is, of course, accidental. A similar change in 1977 (the HO_2 + NO reaction) resulted in an increase in the calculated ozone depletion by a factor of 2. The lesson to be learned is not that nature is inherently stable and kind to the human race, but that we have underestimated uncertainties and that the anthropogenic releases and perturbations seem, at this stage of our understanding, to result in partial cancellation of their effect on the total ozone column. Detailed examples of some of the recent revisions of rate parameters are given below.

While it is hoped that we are in the process of converging on both the correct values of measured parameters and the completeness of the overall reaction matrix, we must guard against excessive optimism. Several general admonitions to experimentalists are in order: (1) Multispecies monitoring schemes should be used whenever possible, especially to verify the identity and formation rates of product species. (2) Experimental parameters such as temperature and pressure need to be varied widely in order to uncover subtle changes in reaction mechanisms. (3) The evaluation of experimental results must include comparison with theory at all levels of rigor, from semiempirical transition-state theory to ab initio quantum calculations. (4) Above all else, vigorous progress in laboratory science must be brought to bear on experimental problems, new techniques must be developed, and greater accuracy achieved.

The following sections present a few examples of chemical and photochemical processes where recent laboratory measurements have differed from earlier ones, resulting in significant changes in model calculations. The examples are broadly subdivided into radical reaction kinetics and photochemical parameters. The chapter concludes with sections on data evaluation and research recommendations.

RADICAL REACTION KINETICS

The description of stratospheric ozone photochemistry in terms of direct and catalytic odd-oxygen removal processes remains unchanged. The pure oxygen, O_x, reaction, $O + O_3 \rightarrow O_2 + O_2$, and its catalytic counterparts, for example, $O + NO_2 \rightarrow NO + O_2$ and $NO + O_3 \rightarrow NO_2 + O_2$, balance the production of O_x from O_2 by solar photolysis in the ultraviolet at wavelengths shorter than 242 nm. The principal catalytic cycles of odd-oxygen species of nitrogen, hydrogen, and chlorine (NO_x, HO_x, and ClO_x) have been frequently described (NRC 1976a,b, 1979, 1982; WMO 1982a) and need not be repeated here. The atomic and radical species involved in these cycles are produced from major and minor atmospheric gases and from some long-lived trace species (N_2O, halocarbons). In addition to taking part in the catalytic cycle reactions, they are transformed into noncatalytic reservoir species (HNO_3, HCl, $ClONO_2$) as well as cross-coupled by a large number of fast reactions.

For the purpose of this update, it is instructive to review the status of six reactions whose rate parameters have been revised as a result of new laboratory data. Furthermore, their revision has had a substantial effect on the results of model calculations.

The Reaction of O with HO_2

The effect of the reaction

$$O + HO_2 \rightarrow OH + O_2, \qquad (1)$$

which is important only in the upper stratosphere where O-atoms are relatively more plentiful, is to remove odd oxygen while converting the less reactive HO_2 into the more reactive OH radical. The latter reacts with HCl to release catalytic chlorine atoms and also reacts with ozone. Reaction (1) thus tends to decrease ozone in the upper stratosphere.

Experimentally, such radical-radical reactions have presented great difficulties in the past, because they involve two different, highly reactive species, both of which must be produced and monitored accurately and sensitively. This has now been successfully accomplished by three groups (Keyser 1982, Sridharan et al. 1982, and Brune et al. 1983) using direct experimental methods rather than modeling a large set of simultaneous steps. The agreement among the three results for the rate constant at room temperature is very satisfactory: (6.1 ± 0.6), (5.4 ± 0.9), and $(5.2 \pm 0.8) \times 10^{-11}$ cm^3s^{-1}, respectively. Keyser has also measured the temperature dependence. At a typical upper-stratospheric temperature of 275 kelvin (K), the recommended value has increased from 4×10^{-11} (NASA 1981) to 6.2×10^{-11} cm^3s^{-1} (NASA

1982). The new measurements represent very real progress in laboratory science, improvement in experimental techniques, and reduction in uncertainty estimates.

The Reaction of OH with HO_2

The reaction

$$OH + HO_2 \rightarrow H_2O + O_2 \qquad (2)$$

is a major loss process for odd-hydrogen (HO_x) species in the middle and upper stratosphere. Its importance in the lower stratosphere was reduced when other HO_x processes (see below) were found to have been underestimated. As a catalyst removal step, it tends to reduce odd-oxygen loss both through the HO_x and ClO_x cycles, but it also increases odd-oxygen loss, since lower HO_x concentrations remove less NO_x, thereby increasing NO_x catalysis.

Experimentally, reaction (2) has been the object of a very large effort over many years. As with reaction (1), direct measurements have been successful only in the past two years. Three low-pressure results have been in good agreement at room temperature: (6.5 ± 2.5), (7.2 ± 1.2), and (6.4 ± 1.5) x 10^{-11} cm^3s^{-1} (Keyser 1981, Sridharan et al. 1981, Temps and Wagner 1982, respectively). No temperature-dependence studies have yet been reported, but preliminary data (Sridharan et al. 1983) indicate a negative dependence. The reaction is extremely fast, yet it appears to exhibit a small pressure dependence, its rate constant rising to 11 x 10^{-11} cm^3s^{-1} at one atmosphere (DeMore 1982). This combination of extreme speed, negative temperature dependence, and positive pressure dependence presents great problems to a satisfactory theoretical interpretation. For application to stratospheric modeling, the recent studies provide a real improvement. They have changed the recommended value from 4 x 10^{-11} (NASA 1981) to 7 x 10^{-11} cm^3s^{-1} (NASA 1982) and have reduced its estimated uncertainty.

The Reaction of OH with HNO_3

The reaction

$$OH + HNO_3 \rightarrow H_2O + NO_3 \qquad (3)$$

is important only in the lower stratosphere, below about 25 km, because HNO_3 is produced in a three-body process that requires higher pressure, i.e., at lower altitude. The reaction removes HO_x species, reduces odd-oxygen removal processes, and thereby increases the ozone concentration, but as in reaction (2), the lower HO_x concentrations result in lower NO_x removal and thereby decrease the ozone concentration.

Experimental studies of the reaction have had a strange history. Two early studies (Margitan et al. 1975, Smith and Zellner 1975) were in very satisfactory agreement, and the issue seemed settled. The rate constant showed a curious temperature dependence, being virtually temperature independent below about 400 K and thereby having an abnormally low preexponential factor. In a more recent study using a different laboratory technique, Wine et al. (1981) found the rate constant to increase with decreasing temperature. Another eight studies confirmed this result (Nelson et al. 1981, Jourdain et al. 1982, Kurylo et al. 1982, Margitan and Watson 1982, Marinelli and Johnston 1982, Ravishankara et al. 1982, Connell and Howard 1983, and Smith et al. 1983). While there is substantial agreement among these more recent studies, the agreement is not complete, with one showing a slight pressure dependence (Margitan and Watson 1982), and another a weaker negative temperature dependence (Connell and Howard 1983). If the rate constant seemed curious on the basis of the 1975 results, it is more so now. The preexponential factor of the rate constant is now less than 1×10^{-14} cm^3s^{-1}, and the effective activation energy is -1.55 kilocalories per mole (kcal mol^{-1}), very unusual values for what should be a simple hydrogen-atom transfer reaction. Intermediate complex formation is suggested, but a satisfactory theoretical description still eludes us. The apparent experimental errors of the early studies at low temperatures can now be rationalized. The consequences of these new results are substantial: at 220 K, corresponding to conditions in the lower stratosphere, the accepted rate constant has been increased by a factor of 4, from 8×10^{-14} to 3.2×10^{-13} cm^3s^{-1}, resulting in much faster HO_x removal and lower ozone loss.

Reaction (3) is a fine example of both pitfalls and progress in laboratory science. It is unfortunate that the experimental errors of the early studies were not recognized. They were subtle, having to do with surface effects due to absorbed or dissolved nitric acid. However, it would also be unfortunate to lose confidence in a large body of other data where such specific problems do not occur.

The Reaction of OH with HO_2NO_2

The reaction

$$OH + HO_2NO_2 \rightarrow H_2O + NO_2 + O_2 \qquad (4)$$

is also likely to be important only in the lower stratosphere where pernitric acid (HO_2NO_2) is expected to be present. (It has not yet been observed in the stratosphere.) The reaction removes HO_x species, as does reaction (3), and thereby both reduces catalytic ozone loss via HO_x catalysis and increases it via NO_x catalysis.

Reaction (3) has been studied experimentally and introduced into models only recently, but its unexpectedly fast rate makes it an important one. There are considerable experimental difficulties in preparing mildly unstable pernitric acid at accurately known concentration so that it can react with OH radicals, but these difficulties have now been mastered. Two earlier studies (Barnes et al. 1981, Trevor et al. 1982) showed some scatter, but are in general agreement with the more accurate, recent work of Smith et al. (1983). Reaction (4) shows a negative temperature dependence, as does reaction (3), but (4) is a factor of 30 to 50 times faster. This underscores again the complexity of stratospheric chemistry: a seemingly unlikely reaction between unstable species becomes potentially interesting and is then found to be fast enough to be very important in the modeling sense which, in turn, stimulates the search for confirmation by field measurements.

The Reaction of O with ClO

The fast reaction

$$O + ClO \rightarrow Cl + O_2 \qquad (5)$$

is the rate-limiting step in the removal of odd oxygen by ClO_x catalysis. Two direct and one indirect measurements made between 1973 and 1977 had led to recommended values of the rate constant of $(5.2 \pm 1.4) \times 10^{-11}$ cm^3s^{-1} at 298 K and an Arrhenius expression of $7.5 \times 10^{-11}\exp(-120/T)cm^3s^{-1}$ (Baulch et al. 1980). In a recent study, Leu (1983) used several different ways of generating ClO and reported a rate constant of 3.5×10^{-11} at 296 K and an Arrhenius expression of $4.8 \times 10^{-11}\exp(-96/T)cm^3s^{-1}$. The recent result reduces the catalytic removal of ozone in the upper stratosphere. Additional laboratory studies of reaction (5) are in progress.

(After this report had been prepared and reviewed, a paper by Margitan [1984] came to our attention. He reports a value for the rate coefficient of $4.2 \pm 0.8 \times 10^{-11}$ cm^3s^{-1} at 298 K, including systematic errors, with no significant temperature dependence.)

The Formation of $ClONO_2$

The effect of the chlorine nitrate recombination reaction

$$ClO + NO_2 + M \rightarrow ClONO_2 + M \qquad (6)$$

is the removal of two catalyst species with the production of a "reservoir" species in the lower stratosphere. Consequently, there is a reduction of ozone loss processes, but its magnitude depends on the removal modes and products of chlorine nitrate. The question posed here involves only its formation rate.

Following its inclusion in computer models (Rowland and Molina 1975, Rowland et al. 1976), the reaction was measured in the laboratory by three groups (Birks et al. 1977, Leu et al. 1977, Zahniser et al. 1977). Although the results were in good agreement, they pertained to the rate of ClO removal, but did not assure that the product was indeed $ClONO_2$. Both experimental (Knauth 1978) and theoretical (Chang et al. 1979a) evidence was later cited that other isomers such as ClOONO, OClONO, and $OClNO_2$ could also be formed and that their subsequent photolysis and reaction rates would likely be very different from that of $ClONO_2$. This problem seems now to have been resolved as the result of diode laser measurements of $ClONO_2$ formation (Cox et al. 1983) and of comparisons of measurements of Cl-atom photolysis yield from $ClONO_2$ (Margitan 1983a) and from the product of the $ClO + NO_2$ reaction (Margitan 1983b). The experimental evidence now favors $ClONO_2$ as the principal reaction product. Reaction (6) provides an interesting example of the interplay of experiment and theory and of the quick response of laboratory measurements to the needs of atmospheric science.

PHOTOCHEMICAL PROCESSES

In the absence of solar radiation, stratospheric reactions would long have reached thermodynamic equilibrium, and so it is only the input of solar energy that keeps the system in nonequilibrium states whose composition needs to be determined. The solar absorption and photolysis processes are therefore the primary perturbing elements of atmospheric chemistry. Experimentally, both the absorption coefficient (or cross section) and the quantum yields and product channels must be determined for each photolyzable species as functions of wavelength over the range of wavelengths of solar radiation that reach the stratosphere.

Three of the nearly fifty radiative processes will be briefly discussed as examples of recent work: the photolysis of oxygen in the Herzberg continuum, the quantum yield of NO_2, and the photolysis products of $ClONO_2$.

Photolysis of Oxygen in the Herzberg Continuum

The photolytic dissociation of O_2 in the wavelength interval 200 to 242 nm

$$O_2 + h\nu \rightarrow O + O(\lambda < 242 \text{ nm}) \qquad (7)$$

is due to a weak, highly forbidden transition from the ground state of O_2 to a weakly bound excited state above its dissociation limit. Because the transition is so strongly forbidden (i.e., the absorption coefficient is so small), it takes a large concentration of O_2 to absorb this radiation, which consequently penetrates well into the stratosphere. While it is true that all of the radiation in this range is ultimately absorbed in the stratosphere, how far it penetrates the stratosphere is important for the altitude profile of ozone formed and the competition of other absorbers, such as chlorofluorocarbons, for the radiation. The latter determines the altitude dependence of chlorine released by photolysis and the magnitude of the consequent ozone removal by ClO_x catalysis.

Experimentally, it is difficult to measure very small absorption coefficients, because very long absorber path lengths (many kilometers) are required at low absorber pressures. Measurements at higher pressures are easily made, but they give larger absorption due not only to the O_2 molecules themselves, but also to O_2-O_2 collision pairs whose contribution is much less important at lower pressures in the stratosphere.

Recent solar flux measurements from 187 to 225 nm (Herman and Mentall 1982, Anderson and Hall 1983) from a balloon-borne gondola give O_2 absorption coefficients 25 to 50 percent smaller than earlier laboratory values. Although in nearly all cases molecular parameters derived from atmospheric experiments are suspect because of the complexity of the atmospheric processes, in this case the field experiment is a straightforward measurement of the transmission of radiation through the atmosphere and the earlier laboratory experiments were so difficult that the new, field-derived values are probably more reliable. A recent laboratory study (Yoshino et al. 1983, footnote to Table 1) supports the field-derived values. However, because the O_2 absorption coefficients are so important to our understanding of the ozone problem, this matter must be explored further.

Quantum Yield of NO_2

The photolysis of nitrogen dioxide (NO_2)

$$NO_2 + h\nu \rightarrow NO + O \qquad (8)$$

is a well-studied reaction of great importance in the troposphere, particularly under polluted conditions, but it is also important in the stratosphere where it affects the NO/NO_2 ratio. The absorption spectrum and cross section of NO_2 have been known with good accuracy for 25 years, but its quantum yield is now undergoing reexamination. The wavelength threshold for photolysis at 398 nm corresponds quite accurately to the ON-O bond energy of the molecule, and at shorter wavelengths the fluorescence intensity drops sharply, because the absorbed energy dissociates the molecule rather than being reradiated. The onset of photolysis is broadened over a wavelength range from 390 to 410 nm due to contributions of thermal internal energy of the NO_2 molecule, but several fairly recent studies (Harker et al. 1977, Davenport 1978) have reported quantum yields of 0.6 to 0.8 in the range 375 to 395 nm, where the lifetime for dissociation would be expected to be very short and the quantum yield should be unity.

The photodissociation rate constant j_{NO_2} has now been measured as function of solar zenith angle at a Colorado field site (Parrish et al. 1983). The quantity j_{NO_2} is the summation over all wavelengths of the product of incident solar radiation intensity, the absorption coefficient, and the quantum yield. These measurements agree with theory only if the quantum yield of NO_2 is close to unity below 390 nm, requiring an upward revision of about 20 percent. This correction is not a large one, and it needs to be verified by laboratory experiments, but it does affect the stratospheric concentration of the active NO_x catalyst species, the most important catalyst group in the stratosphere.

Products of Photolysis of $ClONO_2$

As discussed in connection with reaction (5), chlorine nitrate is an important "reservoir" species for odd chlorine, formed by a recombination reaction in the lower stratosphere and destroyed by photolysis and chemical reaction in several ways. Its impact on stratospheric chemistry depends on the speed and reaction products of these removal steps as well as on its formation rate. Three earlier laboratory studies had given conflicting results regarding its photolysis products. Smith et al. (1977) and Adler-Golden and Wiesenfeld (1981) had reported O + ClONO to be the major products and $Cl + NO_3$ to be unimportant, whereas Chang et al. (1979b) had identified NO_3 to be a major product.

This conflict has now been resolved (Margitan 1983a) by a laser photolysis, resonance fluorescence study of $ClONO_2$ in which the primary atomic products, Cl and O, were measured directly. $Cl + NO_3$ was found to be the major (90 percent) and O + ClONO the minor (10 percent) product channel, and the fast reaction, $Cl + ClONO_2 \rightarrow Cl_2 + NO_3$, whose rate had previously been greatly underestimated, was seen to have been responsible for the earlier discrepancies regarding photolysis products. The current revision has little effect on stratospheric model calculations, but it has helped clarify ClO_x chemistry.

DATA EVALUATION

The large demand for a consistent, reliable base of data for use in computer model calculations has stimulated new national and international efforts to collect and evaluate laboratory data. Until the late 1970s different modelers used different rate or photochemical parameters for the same physical processes--even though compilations of laboratory data by the National Bureau of Standards were available in 1974--and their results were therefore not strictly comparable. To remedy this situation, a panel was established by the NASA Upper Atmosphere Research Program Office in 1977 for the purpose of providing critical tabulations of kinetic and photochemical data. Five evaluations have appeared since then (NASA 1977, 1979a,b, 1981, 1982), and a sixth is in progress. These evaluations have been extremely useful, not only to modelers who use the recommended values in their calculations, but to research scientists who are kept up to date on both results and problem areas in kinetics and photochemistry.

Since 1977 an international CODATA Task Group on Chemical Kinetics has also been active, reviewing, evaluating, and publishing rate and photochemical data for atmospheric chemistry. Two review papers have appeared so far (Baulch et al. 1980, 1982), and a third is in progress. The scope of this effort is being widened, as is that of the NASA panel. For example, while the 1980 CODATA review covered only 148 processes, the 1982 review covered 228. In both the NASA and CODATA panels, updating is being achieved regularly at intervals of from one to two years. These activities are most welcome and important. The evaluations also have the proper mix of full coverage of the experimental data base, brief description of laboratory methods, and critical recommendation of preferred values. The importance of these evaluations cannot be overestimated, and it is imperative that they receive continued support.

RESEARCH RECOMMENDATIONS

If there is one overriding message that emerges from stratospheric research over the past several years, it is that the problem is far more complex than had been thought earlier. The number of chemical and photochemical processes considered has proliferated, transport is poorly understood, the natural background is changing, and the interactions of anthropogenic perturbations with one another and with the shifting natural background may be very nonlinear.

What this means in the context of laboratory measurements is that many more processes need to be measured and understood than had been suggested earlier. There are now many more scenarios regarding total ozone, altitude, and latitude dependence as functions of time and imposed perturbations that require study. Consequently, the sensitivity of the modeled results to the rate parameters is less clearly defined than it was earlier when a single, one-dimensional calculation of the effects of CFC release on total ozone column was of primary concern.

The research needs in laboratory science have therefore been greatly expanded:

- More rate and photochemical parameters must be measured with high accuracy and with careful attention to the identification of product channels.
- The rapid progress in experimental techniques must be maintained, new methods for the detection of reactive species developed, and larger ranges of temperature and pressure variation investigated.
- Experimental work on a host of important elementary processes must be accompanied by theoretical analysis so that these processes are understood and correlated.

The list of required data is likely to grow to 300 parameters and beyond, so that the versatility of experimental techniques will have to be broadened. Although it would be possible to list many reactions where further work is required, such lists would be too long and yet probably incomplete, because the questions are diverse and changing. It is clear, however, that accurately measured rate constants and photochemical data are absolutely essential to our understanding of the problem. The laboratory research program, which fortunately is much less costly than field measurements, needs vigorous support.

3
Field Measurements

INTRODUCTION

This chapter addresses the field measurement of the atmospheric trace species and solar flux as they pertain to the stratospheric ozone problem. These monitoring and expeditionary measurements have been directed toward one or more of three goals:

1. to provide a long-term data base of stratospheric ozone concentrations from which temporal trends can be deduced
2. to provide the input data that are required by the photochemical models being used to predict the response of stratospheric ozone to natural and man-made perturbations
3. to provide data on the chemical species whose concentrations constitute sensitive tests of the validity of the models and their input data

A variety of experimental techniques and instrument platforms has been used with increasing sophistication over the last decade to address these goals. Just as ground-based instruments were supplemented by balloon-borne instruments over this period, the recent years have seen stratospheric aircraft and satellites serve as platforms that can provide extremely valuable global coverage. Combinations of platforms have proven complementary, e.g., high-accuracy, balloon-borne ozone instruments can provide long-term calibrations of satellite sensors. The last few years have also seen the beginning of a program of fundamental importance to atmospheric field measurement research, namely, the assessment of the reliability of instruments and techniques via double-blind intercomparisons in the field.

The stratospheric trace species that is the primary measurement target is, of course, ozone itself. Hence, monitoring in one form or another has been underway for many decades. There is now a long time series of total column ozone measurements. However, the early detection of ozone changes due to man-made causes has focused on seeking trends in height-profile data, since the total column is less sensitive to such perturbations. In the last few years, the Umkehr and satellite data at critical altitudes have been scrutinized intensely. As described in Chapter 5, there are some trends that may be humanly induced, but the interpretations are controversial.

A substantial body of data now documents the tropospheric concentrations of the source gases, CFCs and N_2O, of the stratospheric chlorine- and nitrogen-containing radicals that participate in the catalytic destruction of ozone. The temporal trends have been the recent focus of attention. Similarly the vertical profiles of these species in the stratosphere have been fairly well established for the last few years and have provided a challenge to theory, as is discussed in Chapter 5. The emphasis in recent years has been on determining the stratospheric distributions of (a) other source gases, such as water vapor (H_2O), (b) the multitude of reactive trace species that are involved in ozone chemistry, and (c) the reservoir species, which represent temporary "storehouses" or pathways for removal of ozone-destroying species from the stratosphere by various processes.

In this chapter, we provide brief summaries of the status of techniques and platforms, solar flux measurements, and ozone and other trace species measurements. The emphasis is on developments and results that have augmented or are expected to augment substantially the experimental aspects of potential ozone alterations. Last, based on the experience of the last decade and the current status of atmospheric trace species measurements, we list our recommendations of directions for future research.

EXPERIMENTAL TECHNIQUES AND PLATFORMS

Balloon and Aircraft: In Situ Applications

In situ sampling affords the most direct method of determining the concentrations or mixing ratios of stratospheric constituents at a specified altitude and geographical area. The platform that has been the mainstay of this research has been the high-altitude balloon. For the last decade or so, balloon technology and launch techniques have permitted researchers to explore the stratosphere (up to altitudes slightly higher than 40 km) with payloads of hundreds of pounds, which is a weight that can include a set of multispecies instruments. Furthermore, while the vast majority of balloon launches have been at midlatitudes in the Northern Hemisphere, balloons have been launched at a number of sites around the world, thereby providing some global coverage, albeit limited. Rockets have supplemented balloons for studies at higher altitudes, and aircraft have provided more extensive geographical coverage at lower altitudes.

In spite of the appeal of directness, there are distinct limitations and difficulties associated with such in situ sampling. Clearly, balloons typically allow measurements to be made for only a relatively short time, not much longer than a day. In situ sampling with rockets is, of course, very severely limited in this regard. Furthermore, most balloon flights permit scans only during one ascent and one descent.

In addition to these spatial and temporal limitations, there are fundamental difficulties associated with in situ sampling from any platform. These difficulties follow from the fact that the process of measurement can perturb the sample being taken. For example, the platform can alter the environment in its immediate vicinity, which is the portion of the atmosphere being sampled and which is assumed to be representative of the local atmosphere. Balloons and gondolas can desorb and outgas contaminants and can shade photochemical experiments. In addition, bringing a sample to the vicinity of a detector, the basic objective of in situ measurements, can alter the constituents in the sample. Reactive species in the sample can be lost to the walls of the detector package, and weakly bound species can be dissociated.

A large fraction of the effort that goes into the design of in situ experiments is directed toward minimizing these limitations. There have been notable successes in this regard. Examples of high-quality data sets gathered by in situ techniques are abundant in the recent, detailed review of stratospheric research by WMO (1982a). Nevertheless, as more sophisticated questions are posed regarding stratospheric trace constituents, further innovation in the design of instruments and deployment of instrument packages will be required. Following are short summaries of two recent examples of progress in balloon and aircraft in situ applications.

Reel-Down Balloon Experiment

To circumvent the limitation of most stratospheric balloon flights to two passes through the stratosphere (one each on the ascent and descent), J.G. Anderson and colleagues have devised a balloon experiment in which the instrument package is lowered and raised while the balloon is floating at its maximum altitude (Baum 1982). The instrument package sits on a large winching platform that can be carried to an altitude of about 45 km. The winch's spool contains 20 km of Kevlar line that supports a 400 pound instrument package. The experiment can thereby provide several measurements of the altitude profile during one flight, or can provide continuous measurements at one altitude that is found to be particularly important during the course of a flight. The first test flight (on 15 September 1982, from Palestine, Texas) was a success: an atomic oxygen instrument and diagnostic equipment were let down over a distance of 12 km and reeled up again (J.G. Anderson, Harvard University, personal communication, 1983). Future flights and applications should significantly enhance the role of the balloon in stratospheric research.

U-2 Aircraft: Tropical Stratospheric/Tropospheric Exchange Experiment

The U-2 research aircraft of the National Aeronautics and Space Administration (NASA) provides a platform for in situ measurements in the lower stratosphere. Repeated flights in a selected geographic area can probe a stratospheric phenomenon in depth. An example is the mission in Panama in the summer of 1980 to study the role of tropical cumulonimbus clouds in the transport of water vapor from the troposphere to the stratosphere (Page 1982). The mission coordinated the U-2 aircraft, carrying nine experiments, with a National Oceanic and Atmospheric Administration (NOAA) satellite that could provide infrared images of the area. Eleven flights up to 21 km were conducted in and near convectively active regions. The pilots flew around and over cumulonimbus towers and through the extended anvils in the stratosphere. The measurements have demonstrated the role that such clouds play in transporting water vapor into the stratosphere, where it is the major source of reactive hydroxyl (OH) radicals. The mission is a clear example of the utility of the U-2 aircraft as a platform for lower-stratospheric research.

Balloon, Satellite, and Space Shuttle: Remote Applications

Remote sampling of stratospheric trace constituents has the primary advantage of not perturbing the atmosphere being sampled. Furthermore, since most remote techniques are optical, they have, in varying degrees, the specificity of spectroscopy. Absorption measurements have exploited the long atmospheric path lengths available at sunrise and sunset to detect a variety of stratospheric constituents, many of which are exceedingly difficult to sample in situ. Balloons have deployed such instruments on sun-pointing gondolas. Satellites employing these techniques can provide nearly continuous and global coverage.

The chief limitation of such methods is that the absorption that they measure is an integral along a path of different constituent concentrations and altitudes. The height profile of the concentration of a constituent at a given geographic location, which is often the desired data set, must be inferred from the long-path absorption. While inversion routines can in principle yield these data, the question of uniqueness must be addressed very carefully.

In recent years, several satellites have used such remote sensing methods to measure a dozen or so stratospheric constituents. WMO (1982a) tabulated the types of satellites and the species that they measure. The list is formidable and indicates the great promise that these and future satellite systems, such as the Upper Atmospheric Research Satellite (UARS), have in upper-stratospheric research. Balloon instruments can provide "ground" truth over the long term and the Space Shuttle, with its ability to recover and redeploy satellites, has obvious applications.

The global and nearly continuous coverage of the satellites produces data sets whose size is almost an embarrassment of riches. Namely, in addition to the need to test and verify the observations of these remote instruments, the sheer quantity of data often makes "data assimilation" part of the challenge that satellites present to atmospheric chemists. Nevertheless, several satellite data sets have passed through their periods of internal scrutiny and are now available, in both archives and preliminary publications. We cite examples here, and for each example we briefly summarize one aspect of the recent impact on stratospheric research.

Solar Mesosphere Explorer Satellite: Polar NO_2

The Solar Mesosphere Explorer (SME) satellite was launched on 6 October 1981 (Barth et al. 1983). Among the species measured is nitrogen dioxide (NO_2). A limb-scanning instrument provides data in the altitude range from 28 to 40 km. Mount et al. (1983) have examined the data that were acquired during the winter of 1981-1982 for the pronounced seasonal effect that stratospheric NO_2 exhibits at northern latitudes. Namely, from ground-based measurements, Noxon (1979) has shown that in the winter there is an abrupt drop in the stratospheric NO_2 concentrations at about 45°N. Mount et al. (1983, 1984) have shown that the "cliff" is apparent in the SME data and that it is clear that the abrupt decrease is coincident with the edge of the polar vortex, within which low NO_2 densities prevail. This extensive data set, as well as that from the LIMS satellite (see below), is being used to test a recent theoretical explanation of this phenomenon (see Chapter 5).

Limb Infrared Monitor of the Stratosphere Satellite: Water Vapor

The Limb Infrared Monitor of the Stratosphere (LIMS) satellite (Gille and Russell 1984) provided measurements of several trace species from 20 October 1978 to 28 May 1979. The LIMS data have undergone a lengthy period of internal scrutiny and validation and have now been used to address several atmospheric problems. One of these is the distribution of stratospheric water vapor (Russell et al. 1984). Several features found earlier by balloon-borne instruments have been confirmed by the LIMS data set. The vertical distribution in the tropics shows the presence of a "hygropause" (Kley et al. 1979), where the mixing ratio decreases to a minimum above the tropopause and then increases with altitude. The increase with altitude is less steep in extratropical regions. An important new feature observed in these nearly continuous data is a diurnal variation, which is the largest, 1 to 2 ppm, at the 1 millibar (mb) level. Daytime values are larger than those at nighttime. Further scrutiny of the LIMS H_2O data, and of the diurnal variations in particular, is in progress.

Ground-Based Remote Applications

Remote sampling for stratospheric constituents by ground-based instruments has the advantage of relative simplicity; opportunities for repair, calibration, and adjustment; and no limitations on the time span of observations. These advantages have been used, for example, to explore the seasonal variation of stratospheric constituents. These techniques have been the mainstay of monitoring programs that extended for decades, such as the network of Dobson ozone spectrophotometers. Within the last year, the eruption of the El Chichon volcano has focused attention on the role of interferences, such as sulfur dioxide (SO_2), on ground-based techniques that rely on measurements at only a few wavelengths.

Instrument Intercomparisons

Since the possible threat to stratospheric ozone by man-made chemicals was recognized about a decade ago, there has been a burst of activity in the measurement of trace stratospheric constituents. This activity has been characterized by individual researchers or groups conceiving of a technique wherewith a constituent could be measured, developing the instrument, and applying it in a field measurement campaign. In many cases, an atmospheric constituent has been measured by different techniques applied at different times and places. While the resulting data sets, when pooled, have been extremely valuable in revealing fundamental aspects of the stratosphere, often differences between data sets raise an important question: are the differences reflecting a feature of the atmosphere (e.g., seasonal or spatial variability), or are they due to unrecognized uncertainties in some or many of the measurement techniques being applied to that constituent? One of the most important developments in stratospheric science in the last few years is that instruments that measure a common species are being intercompared in the field as a means of assessing our reliability in making such measurements.

Several federal agencies and private organizations are sponsoring several such intercomparisons for in situ measurements of ozone, remote and in situ data on water vapor, remote techniques for a variety of constituents, and in situ instruments for CFC and nitrous oxide. The intercomparisons are in varying stages. While the international community is involved, these particular programs are being conducted in the United States. European campaigns of this type have also been conducted, and others are being planned. Following is a summary of the results from two of the comparisons.

O_3 Instrument Intercomparison

A variety of ozone instruments and techniques have been used for atmospheric ozone measurements for several years or, in some instances, for decades. While this extensive data set has provided considerable insight into the temporal and spatial behavior of this central atmospheric constituent, the experience gained while making these measurements has revealed many potential shortcomings of the current instruments. An example is the difficulty of reliable measurements near 40 km, where the anthropogenic alteration of ozone is expected to be largest. To assess such measurement problems better, several field intercomparisons have been conducted.

A variety of ozone instruments and techniques were compared during the International Ozone Intercomparison Campaign held in June 1981 in France. The goals, logistics of the campaign, its participants, and the experimental methods that were used have been described by Chanin (1983). The measurements of the total column of ozone by absorption and emission spectroscopy agreed within 10 percent (Matthews and Marche 1983). Lower-altitude (0 to 25 km) sonde measurements exhibited similar differences (Megie and Pelon 1983). Much larger differences were found between measurements made at higher altitudes (Aimedieu et al. 1983). Clearly, additional ozone instrument development is required if humanly induced ozone changes are to be sensitively detected. Much development is underway, and other ozone instrument intercomparisons are in progress.

H_2O Instrument Intercomparison

Large differences exist in the early measurements of stratospheric water vapor (NASA 1979a). To examine the reliability of current water vapor instruments so that future data from different instruments could be used in concert with more confidence, a variety of instruments were intercompared on 7 May 1981, when four balloon payloads were launched from Palestine, Texas, within a period of several hours (NASA/FAA 1981). With only a few exceptions, the resulting water vapor profiles were all within about 1 ppm at altitudes below 25 km and within about 2 ppm at higher altitudes. While such differences were on the order of the combined uncertainties, many of the systematic features of the discrepancies prompted an intensive reinvestigation of the basic properties of each technique and method. In some but not all cases, discrepancies were found that when resolved resulted in improved comparisons. Some refinements have been made in the instruments. The investigators have plans for a second series of intercomparison flights late in 1983 to determine whether stratospheric water vapor can indeed be measured with precision higher than 1 ppm.

OZONE MEASUREMENTS

The existing data base on atmospheric ozone consists of two types: the total amount of ozone above a unit area of the Earth's surface (called the ozone column) and the distributions of ozone concentration with altitude. The bulk of the data is for total column ozone. Only in recent years have significant efforts been devoted to measuring vertical ozone distributions. Much of the early data was gathered for the purpose of understanding upper-atmospheric transport processes. By current standards, the quality of the data is extremely nonuniform. Although recent efforts by international groups, most notably the World Meteorological Organization (WMO), have resulted in significant improvements in data quality, it is still difficult to use existing data for trend analysis and for the detection of possible man-made perturbations.

Ozone distributions can be determined from remote sensing systems and in situ techniques. Remote sensing systems using spectroscopic instruments can be ground- or satellite-based. Satellite systems obviously are of recent origin, providing short temporal records but good spatial coverage. The ground-based system has much longer record, but only at a few geographic locations, with limited vertical resolution. The in situ techniques using various sondes on rockets or balloons give good vertical resolution, but with even more limited geographic coverage and with very poor calibration in the case of rocketsondes. London and Angell (1982) provide a good description and summary of all the observation techniques and the observed ozone variations. Additional details on satellite instruments and their data can be found in WMO (1982a).

Dobson ozone spectrophotometers remain the standard ground-based instrument for measurement of total column ozone and vertical ozone profiles. Other types of ground-based instruments have also been used, but have not contributed much to useful data either because of poor data quality or because of limited deployment (WMO 1981, 1982a,b). Since 1970 satellite-based backscattered ultraviolet (BUV) instruments have gathered more than 10 years of total ozone data with good global coverage. Other satellite-based instruments have also been used, but not to the extent of the BUV instruments. Unfortunately, as was summarized in the WMO reports and in the other publications cited in these reports, there are differences between the ground-based and satellite-based data. Most probably these differences are due partly to systematic drift in satellite instruments.

The distribution of atmospheric ozone is nonuniform both in space and time. Local ozone concentrations vary with altitude, latitude, longitude, and season. The vertical maxima occur in the range of altitudes from 20 to 25 km and with higher concentrations toward the poles. For each hemisphere, the annual cycle has a maximum in spring and a minimum in fall. The Northern Hemisphere has more ozone than does the Southern

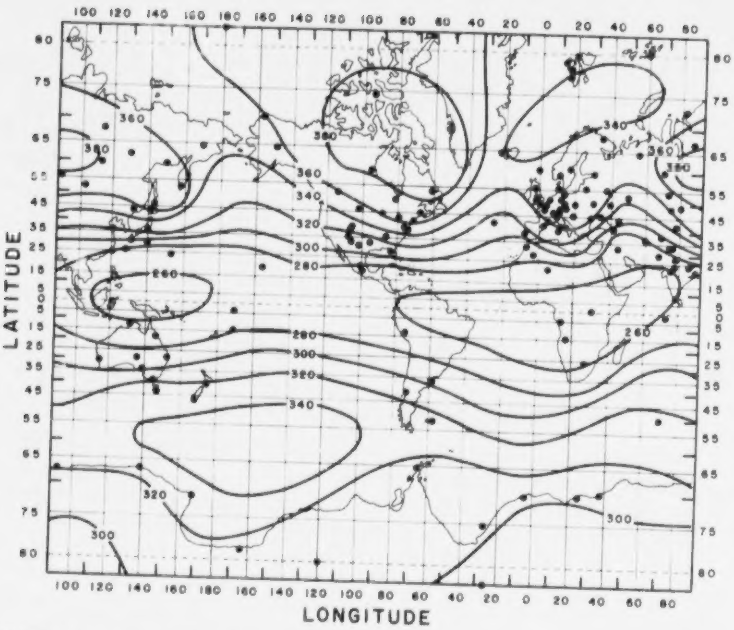

FIGURE 3-1 Average global distribution of total ozone from ground-based data from 1957 to 1975 (in Dobson units). SOURCE: Reprinted, with permission, from London and Angell (1982), The observed distribution of ozone and its variations *in* Stratospheric Ozone and Man, Vol. I, Boca Raton, Fla: CRC Press, © The American Society for Testing and Materials.

Hemisphere. Figure 3-1 shows the average distribution of total ozone both in longitude and latitude derived from 19 years of ground-based observations. The newer satellite observations (Hilsenrath and Schlesinger 1981, Tolson 1981, Miller et al. 1982, Frederick et al. 1983) confirm this picture, while adding more details to the Southern Hemisphere where ground observations are limited. It is clear that variations in total ozone with longitude are considerably less than the variations with latitude. Figure 3-2 illustrates the latitudinal variation in zonally averaged total ozone with season. Other natural variations in total ozone with differing temporal frequencies have also been studied (Guthrie 1983, Hasebe 1983). Although these variations may be of significance in understanding the stability of the ozone layer, their

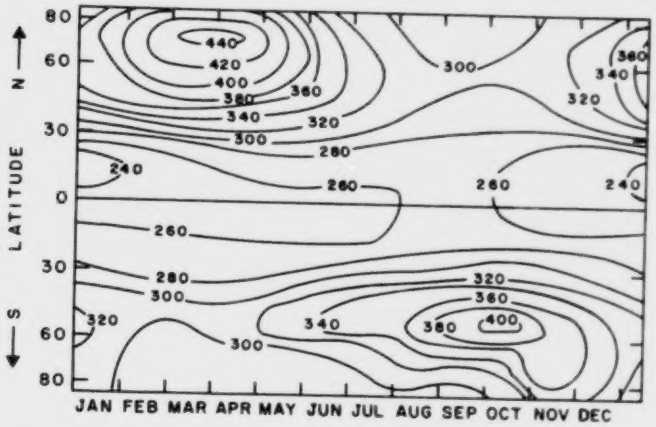

FIGURE 3-2 Latitudinal and seasonal variation of the average total ozone from ground-based measurements between 1957 and 1975. SOURCE: Reprinted, with permission, from London and Angell (1982), The observed distribution of ozone and its variations *in* Stratospheric Ozone and Man, Vol. I, Boca Raton, Fla: CRC Press, © The American Society for Testing and Materials.

contributions to long-term and global variations appear to be small.

Figure 3-3 illustrates the average height-latitude cross section of the ozone partial pressure expressed in nanobars (nb). The distributions shown represent approximately the time averages of 10 years of data from 1966 to 1976. In general, there is relatively little ozone in the troposphere except for the polar and subpolar upper troposphere. This should not be confused with the oxidants (mostly ozone) found in high concentrations in the polluted urban environments. Analysis of the data in Figure 3-3 shows strong latitudinal transport with resultant large fluctuations in the lower stratosphere just below the ozone maxima (London and Angell 1982). It is distributions of this type that modern theory of stratospheric chemistry attempts to explain, studying how they may be perturbed by human activities.

OTHER TRACE SPECIES MEASUREMENTS

A substantial body of data now exists for numerous species in the stratosphere (WMO 1982a). Some of it is

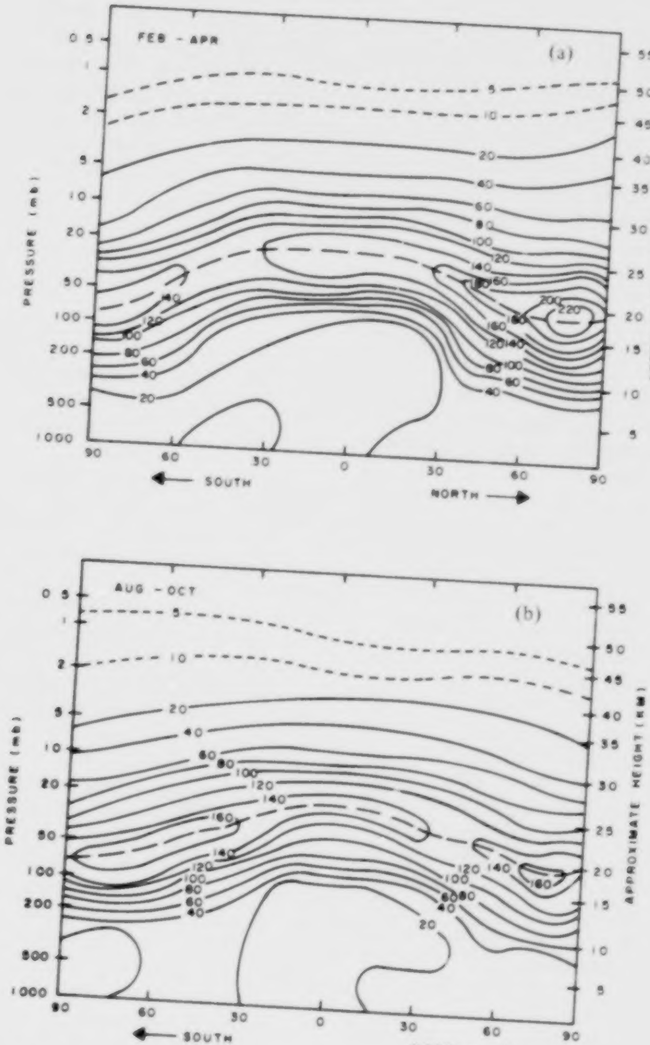

FIGURE 3-3 Partial pressure (mb) of ozone as a function of latitude and altitude for (a) February through April and (b) August through October. Dashed line between 17 and 26 km indicates maximum partial pressure. SOURCE: Reprinted, with permission, from London and Angell (1982). The observed distribution of ozone and its variations *in* Stratospheric Ozone and Man, Vol. I, Boca Raton, Fla: CRC Press. © The American Society for Testing and Materials.

adequate to test aspects of stratospheric models (see Chapter 5). However, in many instances the data are still woefully inadequate. The measurements that have been made in the last year or so may be characterized as being more of supportive or augmentive nature than of a revolutionary nature. Here we briefly summarize the status of three classes of trace species and note the recent developments in each.

Source Gases

Tropospheric Concentrations

Trends in tropospheric gases that are the major source species for stratospheric radicals are now better documented. Some controversial aspects still remain, however.

CFCs. Several long-term monitoring programs have addressed the trends of these species, the most extensive being that of NOAA's Geophysical Monitoring for Climatic Change Laboratory (GMCC) and the Atmospheric Lifetime Experiment (ALE). The GMCC program began in 1975. It provides global coverage by flask sampling at (presently) 21 sites, followed by gas-chromatographic analysis at a central laboratory. The primary goal of the program is to determine long-term trends. Recent GMCC data for CFC-11 suggest that the well-documented annual increase in atmospheric concentrations may be lessening (J. Peterson, NOAA GMCC, personal communication, 1983), as expected from the decreased release rates. The ALE program has acquired data since July 1978 and has published the data obtained through June 1981. It provided relatively precise and accurate measurements at 5 sites by equipping each with an onsite gas chromatograph. The emphasis of the ALE program has been on determining lifetime estimates, which are discussed in detail in Chapter 5. The trends observed for other chlorine-containing gases are reviewed in Chapter 5.

N_2O. Several data sets now support the temporal increase in the atmospheric concentrations of N_2O that was first noted by Weiss (1981). Both GMCC (J. Peterson, NOAA GMCC, personal communication, 1983) and ALE (Prinn et al. 1983a,b) show increases. Khalil and Rasmussen (1983a) report hemispheric and seasonal variations in the increase, as noted from three years of data. Both natural and anthropogenic sources have been proposed, but these remain speculative at the present.

$\underline{CH_4}$. An important discovery in the last year or so is the fact that the tropospheric concentrations of methane are increasing at a few percent per year (Rasmussen and Khalil 1981). These atmospheric observations have been supported by ice-core measurements of Craig and Chou (1982), who find that the increase experienced in the period 1965-1980 is a dramatic one compared with the much more modest increase of the past hundred years. Recent measurements (Khalil and Rasmussen 1983b) indicate that there are seasonal variations in CH_4 concentrations. Because of the important role that this species plays in the atmospheric "greenhouse" effect as well as in chemical reactions, considerable effort is focused on understanding its sources and sinks (see, for example, NRC 1983).

Vertical Profiles

Very few measurements of the stratospheric profiles of the long-lived source species have been made in the last year or so. This has not proven to be a handicap, however. The existing profiles of the CFCs, N_2O, and CH_4 have proven sufficient to test the revised model predictions of these profiles (see Chapter 5). Data from the Stratosphere and Mesosphere Sounder (SAMS) satellite (Jones and Pyle 1984) support the general features of these profiles, and global and nearly continuous temporal coverage has revealed some seasonal variations.

The stratospheric concentrations of water vapor have become better defined in the last year or so, but as a result several puzzling questions have been raised. Mastenbrook and Oltmans (1984) have continued to monitor stratospheric water vapor and have shown that the concentrations vary substantially with time for reasons that are not understood. Furthermore, Kley et al. (1982) have shown that water vapor exhibits a minimum in concentration a few kilometers above the tropical tropopause, which calls into question the belief that the flow of water vapor into the stratosphere is controlled solely by the tropical tropopause temperature (see Chapter 4). Several fundamental questions about the altitude and latitude variations of stratospheric water vapor are unanswered (Ellsaesser 1983).

Radical and Reservoir Species

Radicals

The recent observations of the stratospheric radical species are summarized here by the principal catalytic cycles.

Nitrogen. The satellite observations of NO_2 have been described above. Other studies have also augmented the existing picture of the behavior of this species. The ground-based studies by McKenzie and Johnston (1982) made in the Southern Hemisphere are in good agreement with the seasonal and diurnal variations seen in the Northern Hemisphere.

Chlorine. The approximate abundance and vertical distribution of daytime stratospheric ClO have been reported in several earlier in situ and remote studies, and these data are summarized by WMO (1982a). However, the measurable presence of ClO in the stratosphere has been called into question recently. Mumma et al. (1983) carried out a ground-based search for the lines of ClO using an infrared heterodyne spectrometer in the solar absorption mode. None were observed, and an upper limit for the integrated vertical column density of 2.3×10^{13} molecules cm^{-2} was reported. This value is a factor of 7 less than is indicated by the previous measurements.

An additional ClO investigation has been conducted since the study of Mumma et al. (1983), and these results support the earlier observations of this radical. Solomon et al. (1984) have continued their earlier (Parrish et al. 1981) ground-based, millimeter-wave spectroscopic studies, this time at Mauna Kea, Hawaii, where atmospheric water vapor, which dominates tropospheric absorption of stratospheric emission lines at millimeter-wave frequencies, can be very low and stable. The results not only support their earlier ground-based studies and the in situ investigations, but also demonstrated the expected day-to-night variation. Thus, with the one exception, the current experimental observations of ClO are generally consistent with the predictions of current models. Because of the central role that ClO plays in the ozone-chlorine chemistry, it is important to resolve the difference between methods. An intercomparison of ClO measurement techniques seems to be in order.

Hydrogen. There are relatively few in situ measurements of OH, as the review by Anderson (1980) demonstrates. Yet, this radical plays a critical role in stratospheric chemistry. In the last few years, there have been additional studies, but the measurement status for OH is still not yet as satisfactory as its role requires.

Heaps and McGee (1983) have reported two measurements from a balloon-borne laser radar system. Their results are two to five times smaller than earlier resonance-fluorescence measurements (Anderson 1976), and the diurnal variation is not as large as expected from the photochemistry. Pyle et al. (1983) recently have used LIMS satellite data for NO_2 and HNO_3 to deduce a height profile for OH. Since the method employs the ratio of these species, many of the measurement uncertainties largely cancel. The resulting profile yields midday values from 26 to 40 km with an estimated accuracy of 40 percent. These values lie between the direct measurements of Anderson (1976) and those of Heaps and McGee (1983).

The in situ measurements of stratospheric HO_2 are even more limited than those of OH. Two sets of data exist; one made by j matrix-trapping, followed by laboratory spin-resonance analysis (Mihelcic et al. 1978) and another by resonance fluorescence (Anderson et al. 1980). Ground-based measurements of HO_2 that can complement the earlier in situ studies have recently been made.

De Zafra et al. (1984) have used a sensitive millimeter-wave receiver to obtain HO_2 emissions line profiles. A class of HO_2 altitude profiles from recent photochemical models were compared to the observed line shapes. The best match was an altitude profile that appears to be inconsistent with the in situ data, the latter being substantially larger. The millimeter-wave spectroscopic study is most sensitive at altitudes above those where the in situ data were gathered, but the two data sets do not join smoothly.

While there is still considerable uncertainty in the current status of stratospheric OH and HO_2, it is very gratifying to see that these important radicals are now being addressed by a variety of experimental methods.

Reservoirs

Arijs et al. (1982) have continued to deduce HNO_3 concentrations between 20 and 25 km from observed ion concentrations. The data are within the variation observed between earlier studies, which, unfortunately, is large. Williams et al. (1982) have extended their nitric acid column-density measurements to include Antarctica. The general trend of increasing column densities with increasing southern latitude is consistent with the observations in the Northern Hemisphere.

Little has changed since the last review (NRC 1982) regarding the status of the stratospheric concentrations and roles of the short-lived radical and reservoir species (HCl, HO_2NO_2, $ClONO_2$, N_2O_5), which probably testifies to the difficulties of making such measurements. The few new measurements support earlier data sets and we note those here. Other new studies represent promising new starts. Roscoe (1982) has recently reported a tentative observation of nitrogen pentoxide (N_2O_5), which is an important reservoir molecule, particularly so since Solomon and Garcia (1983a) have identified it as the odd-nitrogen reservoir in the polar winter. The preliminary estimate of the rate of increase of N_2O_5 after sunset is in good accord with the range of values predicted by models (Solomon and Garcia 1983a). These measurements should be refined and extended. There are very few studies of these short-lived reservoir species, which pose formidable measurement difficulties.

RESEARCH RECOMMENDATIONS

Over the last decade, a great deal of data on the distributions of stratospheric trace species has been obtained, and has led to a substantial improvement in our understanding of the potential of inadvertent alteration of the stratosphere by human activities. The complexity of the coupled chemical-radiative-dynamical atmospheric system has been better appreciated, but the reasons for understanding it have only been reinforced. Hence, the need for a wide variety of accurate information regarding stratospheric trace species is stronger than ever. Successful research tracks must continue to be pursued and new initiatives started. Some of the more obvious of these are the following:

- The long-term monitoring of the atmospheric concentrations of the source gases must be supported, because the worth of such data depends strongly on the continuity of the record. Particular emphasis should be placed on the integrity of standards, international intercomparison, and publication of the data, accompanied by documentation of the methodology.

- Instrumentation should be developed to measure ozone concentrations at 40 km with accuracy of a few percent so that there can be early detection of trends at the altitude where the percentage ozone changes due to anthropogenic perturbations are calculated to be the largest relatively. A monitoring program should then be instituted. The thrust should be toward a combination of balloon and satellite sensors.
- The development and field testing of instrumentation to measure a variety of stratospheric trace species should be supported strongly since many of the important species remain unmeasured or poorly measured. The primary goals should be the radical and reservoir species.
- A field program designed to define how water vapor enters the stratosphere and to determine the global aspects of the distributions of this poorly defined source gas should be organized.
- The discrepancies between ClO measurements taken with different techniques should be resolved as soon as possible.
- Rigorous, double-blind intercomparisons of instruments in the field should be continued to assess the reliabilities of current technology, since this is the best way to assess accuracy. Support is critical during the difficult phase of this endeavor, namely, after differences have been demonstrated and rationalizations are then sought.
- Intensive measurement campaigns should be mounted to deploy a group of multiple-species instruments that can determine the full data set required to test a proposed hypothesis. The campaigns should include ground-based, balloon, aircraft, and satellite configurations.

4

Meteorological Processes

INTRODUCTION

Atmospheric motions are among the most complex and least understood of the factors that control the amount and distribution of stratospheric ozone. Transport by structured meteorological systems partly controls the distribution of the long-lived and intermediate-lived trace species that are important for the photochemistry of ozone. This meteorological control, which is especially important in the lower stratosphere, implies that photochemical models of the ozone layer must take proper account of meteorological processes.

The role of motion is not, however, simply to transport and diffuse ozone and other trace substances in a passive manner. The winds in the stratosphere are in approximate geostrophic balance (i.e., the horizontal winds blow parallel to the isobars with speed proportional to the cross-stream horizontal pressure gradient). The mass distribution is in hydrostatic balance (i.e., temperature is inversely proportional to the rate of decrease of pressure with height). Since both wind and temperature are related to the three-dimensional distribution of pressure, they are related to each other. This coupling of the wind and temperature field (referred to as the "thermal wind" relation by meteorologists) implies that changes in the wind distribution are not independent of temperature changes. Thus, since both radiative and photochemical processes are temperature dependent, there is a very complex coupling among dynamics, radiation, and photochemistry in the stratosphere.

Recent analyses of temperature and ozone data from several satellite experiments have revealed unexpectedly large variability in the winds and temperatures in the winter stratosphere of the Northern Hemisphere. This variability, which occurs on time scales varying from subseasonal to multiannual, has important consequences for the transport of trace species, and must also be carefully considered in analyses of trends in ozone.

Progress has recently been made in the theoretical understanding of the nature of transport and the manner in which net transport is related to meteorological processes (Mahlman et al. 1983). A reasonable conceptual model of transport is beginning to emerge, but difficulties remain in translating the concepts into quantitative parameterizations of transport phenomena for use in photochemical models. A key part of the transport issue that is not well understood is the distribution of tropospheric source species and the physical mechanics for their transfer into the stratosphere. The observed extreme aridity of the stratosphere, which indicates that tropospheric air must be nearly completely dehydrated as it enters the stratosphere, places severe constraints on models for exchange of trace species between the troposphere and stratosphere. No satisfactory resolution of this problem is yet available.

Finally, meteorological processes are also coupled to ozone perturbations through radiative-dynamical coupling that may affect the climate at the ground. This aspect has recently received attention in light of concerns about potential effect on global climate from the observed trend in the atmospheric concentration of carbon dioxide.

VARIABILITY

Subseasonal Variability and the Sudden Warming

Subseasonal variability in the Northern Hemisphere stratosphere has been studied with the aid of conventional radiosondes for the past 25 years and with satellites for the last decade. The nature of planetary-scale disturbances in the stratosphere has been well documented. For the ozone perturbation problem, the most significant aspect of the observed variability is the occurrence of large fluctuations in the amplitude of planetary-scale disturbances in the winter stratosphere. Recent research (e.g., McIntyre and Palmer, 1983) indicates that much of the poleward and downward transport of trace species occurs in the winter and spring seasons in association with episodic wave-induced mixing events rather than as a result of weak background turbulent diffusion.

The most spectacular example of such episodic mixing is the complex phenomenon called the "sudden stratospheric warming." Major sudden warmings, which occur irregularly about once every year or so, can lead to temperature rises of 30 K or more over the entire polar stratosphere on time scales of a few days. The dynamics of such warmings have been elucidated recently with the aid of a variety of new theoretical tools. (See McIntyre [1982] for a review and extensive references to recent observational and theoretical work.) It is now clear that warmings are initiated when the distribution of the zonal mean flow in the stratosphere is favorable for guiding vertically propagating planetary-scale waves that are generated in the troposphere upward into the polar stratosphere. The viscous drag that such waves exert on the stratosphere causes a deceleration of the winds in the polar night vortex, rapid poleward and downward transport of heat and mass, and a warming in the polar region. Similar processes operate during the abrupt "final warming" that generally marks the transition from a winter to a summer circulation regime in the stratosphere. There can be little doubt that such warmings produce enormous enhancement of the normal transport processes and thus must be important for the climatology of ozone and other long-lived trace species. Although limited observations of ozone are available for the 1979 sudden warming from the infrared radiometers on Nimbus 7, no systematic studies of tracer transport during sudden warmings have yet been attempted. The well-known spring ozone maximum at high latitudes is consistent with enhanced transport during the winter season. Unfortunately, the only relatively long-term global ozone measurements have been made with satellite-based solar ultraviolet backscatter techniques, which provide no information in the polar night. As a consequence, the variability of ozone in the winter stratosphere at high latitudes remains poorly known.

Interannual Variability of Temperature Profiles

Perhaps of more significance than the subseasonal variability, at least for the ozone perturbation problem, is the recently discovered large-amplitude year-to-year variability of the temperature in the winter stratosphere.

There are now more than 10 years of satellite radiometer data available for analysis of the temperature structure of the stratosphere. These data include low vertical resolution operational data analyzed by the U.S. National Meteorological Center (NMC) and the British Meteorological Office (BMO), as well as higher-resolution data from several experiments in the Nimbus satellite series. Analyses of various subsets of these data have been recently reported by Hamilton (1982), Smith (1983), and Geller et al. (1983). These analyses indicate that monthly mean temperature and zonal wind distributions in the winter stratosphere may differ dramatically from year to year. At present, the extent to which this observed variability is directly forced by tropospheric motions or might be attributed to internal instabilities of the stratospheric circulation is not known. The existence of such dramatic (and unexpected) variability in the circulation suggests that similar variability must exist in the net poleward and downward transport of ozone and other trace species. Since this transport must represent a major sink for stratospheric ozone, an understanding of the sources, magnitude, and temporal and spatial distribution of the interannual meteorological variability is required to evaluate the adequacy of the treatment of transport processes in photochemical models. It is also apparent from current data that 10 years is not a sufficiently long period to establish a temperature climatology for the winter stratosphere. The year-to-year variability of stratospheric temperature profiles is simply too great. If, as seems probable, the natural year-to-year variability is of similar magnitude in the ozone distribution of the winter stratosphere, then great care must be exercised in evaluating ozone trends. Statistical models that take no account of the "red noise" character of atmospheric motions (i.e., the tendency for the amplitude of the variance to increase with period) must be used with great caution.

The satellite temperature climatology developed to date is limited to only a few winter seasons. The large observed interannual variability revealed in these data suggests that routine observations of the winter stratosphere will be needed for many years in order to establish a climatology, to understand the sources of interannual variability, and to clearly establish the existence of trends. For example, the interannual variability in the polar stratosphere during the 1970s has been attributed to interaction with the quasi-biennial oscillation of the equatorial stratosphere by Holton and Tan (1982) and to variations in tropospheric forcing due to the so-called Southern Oscillation (Van Loon et al. 1981). Currently available data are not adequate to clearly distinguish between these two very different alternatives. Similarly Hasebe (1983) has linked the interannual variability of total ozone during the 1970s to both the equatorial quasi-biennial oscillation and to the Southern Oscillation. Although the quasi-biennial oscillation is sufficiently regular that responses to it may be relatively easily removed from the data for the purpose of trend analysis, the Southern Oscillation is quite irregular and has a sufficiently red spectrum (i.e., the amplitude increases with increasing period) so that natural ozone fluctuations linked to it will be difficult to separate from perturbations caused by human activities until long-term satellite-based measurements of temperature and ozone become available.

The problem of variability is most severe in the lower stratosphere. This region is, of course, also where chemical and dynamical time scales are similar, and where current models suggest that very involved chemical processes should lead to ozone increases that approximately balance the calculated decreases at higher elevations. Thus, the current calculation of a small net change in the total column ozone--as in the case of the much larger 1979 result--is based on the assumption that the one-dimensional models provide an adequate approximation for the slow chemistry in the lower stratosphere despite the complex meteorological processes that occur in that region.

MODELING THE WINTER STRATOSPHERE

The observational data already existing, although inadequate to define a long-term climatology properly, do provide important constraints for verification of three-dimensional models of the general circulation of the global atmosphere. Until very recently general circulation models of the middle atmosphere have had only a very limited success in simulating the winter distributions of polar temperature and wind. Nearly all models produce much lower temperatures and stronger zonal velocities than are observed. The overly strong zonal jets that typically are produced by middle-atmosphere circulation models indicate a very serious deficiency in the models.

Because of the coupling of large-scale wind and temperature fields through the thermal wind balance, unrealistic winds imply unrealistic temperatures, and transports therefore are likely to be in error.

A marked improvement in simulation of the thermal balance of the polar region has been obtained by the National Center for Atmospheric Research (NCAR) Community Climate Model (Pitcher et al. 1983), although it contains only marginal resolution in the stratosphere. The improved simulation in this model may be partly attributed to its novel formulation of radiative processes. However, mechanical damping apparently also plays a role. In any case, the NCAR model does produce an improved simulation of the climatology for the lower stratosphere. Similar improvements for models that adequately resolve the stratosphere and mesosphere will almost certainly not be made on the basis of improved radiative algorithms alone. It has been suggested recently that wave drag and diffusion due to breaking of internal gravity waves may provide an essential momentum sink for the stratosphere (Mahlman and Umscheid 1983). Without such wave drag, the mean winds would almost certainly be much stronger than observed, as is confirmed by general circulation models that omit wave drag (Mahlman et al. 1983). Because of the sensitivity of vertical propagation of stationary tropospheric planetary-scale waves to the mean wind distribution, models that simulate the mean wind poorly will also simulate planetary waves poorly, and are thus unlikely to model the observed variability properly.

Lindzen (1981) has suggested a simple parameterization for wave breaking that can be used in numerical models. Holton (1982b) has shown that this parameterization works well in a simple model. However, further progress in parameterizing wave drag and diffusion for global models appears to require a substantial observational effort to obtain a gravity-wave climatology. Such an effort is essential because adequate modeling of the motions of the stratosphere requires accurate specification of the background mean winds, which in turn requires accurate modeling of the distribution and magnitude of the wave drag and diffusion. Fortunately, the development of the so-called MST (Mesosphere-Stratosphere-Troposphere) radars that can provide wind measurements with fine temporal and spatial resolutions provides a powerful ground-based observing system for defining the physical characteristics and temporal and spatial distribution of gravity waves and turbulence (Balsley and Gage 1980), and increasing efforts to establish a gravity-wave and turbulence climatology for the stratosphere can be expected in the near future.

TROPOSPHERE-STRATOSPHERE EXCHANGE AND TRANSPORT

The exchange of trace species between the troposphere and the stratosphere is one of the essential steps in the ozone perturbation process. Most of the key species involved in the perturbation chemistry have their sources in the troposphere and must be transported to the stratosphere to participate in the complex chemistry of the ozone layer.

The simplest qualitatively plausible model for troposphere-stratosphere exchange consists of bulk advection by a single mean meridional circulation cell in each hemisphere with uniform rising motion across the tropical tropopause, poleward drift in the stratosphere, and by continuity of mass, a return flow into the troposphere in the extratropics. Such a circulation was proposed by Brewer (1949), who argued that a scheme in which the upward-moving air passed through the "cold trap" of the high, cold, tropical tropopause seemed to be required to explain the observed low mixing ratio for water vapor in the stratosphere. Somewhat later, Dobson (1956) pointed out that the poleward and downward portion of this mean circulation was qualitatively consistent with the observed high concentration of ozone in the lower polar stratosphere, far from the region of photochemical production. Although the Brewer-Dobson cell provides a useful partial model for troposphere-stratosphere exchange and transport in the stratosphere, it clearly does not represent a complete physical description of exchange.

Evidence that the Brewer-Dobson cell model is an oversimplification has come from two types of observational studies. On the one hand, diagnostic studies of the Eulerian mean meridional circulation in the winter stratosphere have revealed a two-cell pattern with rising motion in the tropics and polar regions and descending motion in midlatitudes. On the other hand, observational studies of the transport of ozone and radioactive tracers have revealed that large-scale eddy motions play an important part in tracer transport. The comparative roles of the eddies and the Eulerian mean are somewhat obscured by the fact that there often tends to be almost complete cancellation between eddy transport and mean flow transport.

When the mechanisms of exchange in midlatitudes are considered, however, there can be little doubt that eddy processes dominate. Observations reveal that the transfer of trace constituents from the stratosphere to the troposphere is concentrated in midlatitudes and is dominated not by the mean circulation, but by mesoscale eddy processes associated with generation of cyclonic and anticyclonic disturbances in the troposphere. Case studies of radioactive tracers and dynamical tracers (potential temperature and potential vorticity) in the vicinity of the tropospheric jet stream indicate that considerable stratospheric air is mixed into the troposphere by intrusions that occur in conjunction with the development of upper-level frontal systems (Danielsen 1968, Shapiro 1978). These intrusions, which occur in thin layers with horizontal- and vertical-scale lengths of 100 and 1 km, respectively, are eventually destroyed by irreversible vertical mixing in the troposphere (Shapiro 1980). Although some tropospheric air no doubt is mixed into the stratosphere by slow meridional circulations associated with the jet stream, the extreme dryness of stratospheric air suggests that the primary transport of mass from the troposphere into the stratosphere indeed takes place in the equatorial region in accordance with the Brewer-Dobson model.

In the past few years, much progress has been made toward resolving the relative importance of eddy motions and mean cell motions. The major contribution to this resolution has been the work of Andrews and McIntyre (1976, 1978), who stressed the fundamental difference between Eulerian zonal averages and Lagrangian averages. Dunkerton (1978) used the Andrews and McIntyre framework to show that the Brewer-Dobson circulation should be interpreted as a Lagrangian mean mass circulation, and that to a good approximation this circulation could be approximated by the "diabatic" circulation. The latter circulation is the mean meridional circulation for which the adiabatic heating/cooling due to the mean vertical motion just balances the zonal mean diabatic cooling/heating. Since the lower stratosphere is radiatively heated at low latitudes and radiatively cooled at high latitudes, the diabatic circulation (shown schematically in Figure 4-1) is consistent with a mass circulation in which air flow from the troposphere into the stratosphere is limited to the tropics.

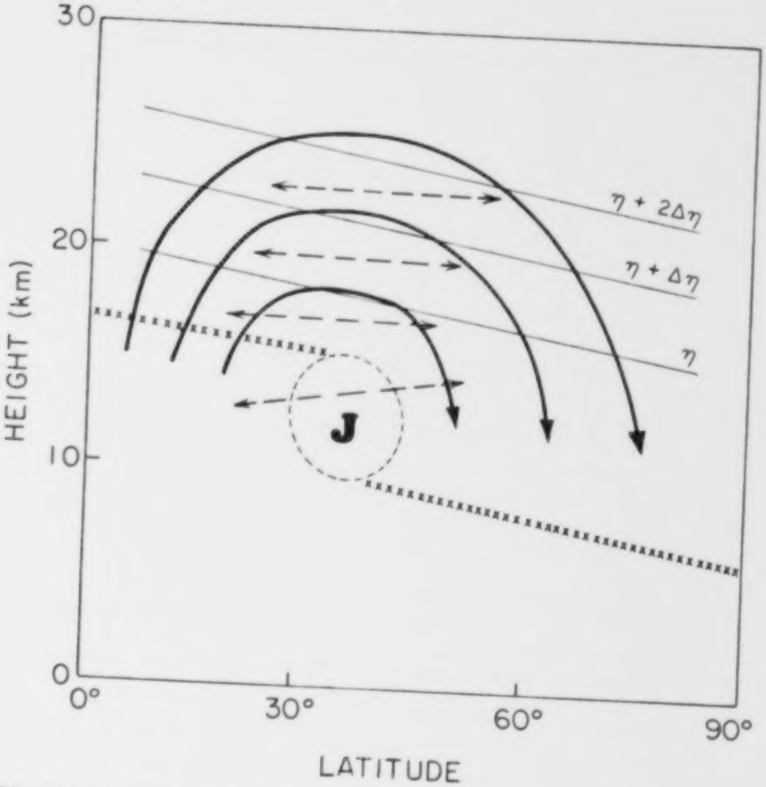

FIGURE 4-1 Schematic diagram of transport in the lower stratosphere. Heavy arrows show Brewer-Dobson circulation. Dashed arrows indicate quasi-isentropic mixing by eddies. Mean tropopause is indicated by crosses, and J indicates mean jet stream. Light lines labeled with mixing-ratio values (η) show mean slope of a long-lived vertically stratified tracer.

However, as Mahlman et al. (1983) has stressed, the combination of upward advection in the tropics and downward advection at higher latitudes implied by the diabatic circulation would cause the mean isopleths of vertically stratified tracers to slope steeply downward from equator to pole. Although tracers such as methane and nitrous oxide do have isopleths that slope in this sense, the actual slopes are much less than those implied by a balance between the advection by the diabatic circulation and photochemical destruction. The additional process required to explain the observations is rapid meridional mixing by quasi-isentropic eddies. This process is demonstrated clearly in the simulation studies of Levy et al. (1979). Thus, as summarized in Figure 4-1, the gross characteristics of stratosphere-troposphere exchange and transport within the lower stratosphere can be modeled in terms of a combination of a mean diabatic circulation and quasi-isentropic mixing by eddies.

Although there can be little doubt that the freeze-drying of air due to upward passage through the tropical cold trap is a qualitatively reasonable explanation for the extreme dryness of the stratosphere, recent observations have revealed a number of problems with the Brewer-Dobson cell hypothesis. Measurement of water vapor in the stratosphere is extremely difficult experimentally. Attempts to summarize measurements from a variety of sources have been made by Harries (1976), Robinson (1980), and Ellsaesser et al. (1980). The bulk of current evidence suggests a mean mixing ratio in the lower stratosphere of about 4 ppm. Dehydration to such a low mixing ratio would require that air entering the stratosphere pass through a cold trap with a temperature less than 191 K at 100 mb, and that such air not carry ice crystals into the stratosphere, so that the total water content would be limited by the saturation mixing ratio at those conditions.

Climatological data, however, indicate that for much of the tropics, even in the active intertropical convergence zone (ITCZ), the temperatures at the tropical tropopause are insufficiently cold to allow freeze-drying of air to a mixing ratio of 4 ppm. An additional difficulty with the Brewer-Dobson hypothesis was revealed by the vertical profiles of the water vapor mixing ratio obtained during the 1980 Panama experiment carried out by NASA (Kley et al. 1982). These profiles reveal a distinct minimum in the mixing ratio at 19 km (well above the tropopause). This minimum is significantly smaller than the saturation mixing ratio at the tropopause level. Thus, it seems clear that the water vapor mixing ratio profile in the Panama region cannot be explained on the basis of local vertical transport processes. Rather, long-range quasi-horizontal transport must be invoked to account for the minimum at 19 km.

Newell and Gould-Stewart (1981) suggested that the stratospheric water vapor observations are consistent with a model, which they called the "stratospheric fountain," in which most of the flux of mass from the troposphere into the stratosphere is concentrated in relatively limited regions of the tropics where tropopause temperatures are observed to be significantly colder than those at Panama during the summer. They found that 100-mb temperatures less than 191 K are generally limited to the Indonesian "maritime continent" during the Northern Hemisphere winter, and to the Indian monsoon region during the Northern Hemisphere summer. Atticks and Robinson (1983) utilized the enhanced network of tropical soundings developed for the Global Weather Experiment in 1979 to examine further the temporal and spatial distribution of tropopause temperatures. Their results were generally in accord with those of Newell and Gould-Stewart; however, they argued that during the Northern Hemisphere winter sufficiently cold tropopause conditions occurred over a broader range of longitudes than suggested by Newell and Gould-Stewart. In any case, it is clear that the tropical tropopause is, on the average, highest and coldest in both hemispheres during the Northern Hemisphere winter. Only in the Asian monsoon area are conditions favorable for freeze-drying air to the observed stratospheric mixing ratios during the Northern Hemisphere summer.

The stratospheric-fountain hypothesis does not itself provide a dynamical mechanism for assuring that air passing through the cold trap will have its water content reduced to the saturation mixing ratio at the tropopause. The occurrence of strong convection penetrating into the lower stratosphere in the Indonesian region during the Northern Hemisphere winter has been amply documented in the Winter Monsoon experiment (Johnson and Kriete 1982). Thus, overshooting cumulus turrets would tend to carry ice crystals into the stratosphere, so that the immediate effect of cumulus penetration should be to hydrate rather than to dehydrate the stratosphere.

To understand the dehydration of the stratosphere more completely, it appears necessary to consider the dynamical and microphysical processes that occur over the full life cycle of tropical convective systems. It is well known that the sinking due to negative buoyancy that follows the overshooting of cumulonimbus turrets in the tropics produces massive cirrus anvil clouds, far larger than those produced at midlatitudes (Danielsen 1982a, Johnson and Kriete 1982). Such anvils may last for 5 to 10 hours or more. Measurements of stratospheric aerosols by Knollenberg et al. (1982) during the 1980 Panama experiment indicated that up to 40 percent stratospheric air may be entrained into the collapsing turrets that form the anvil clouds. Thus, the mean potential temperature in the anvils must exceed that of the convective turrets, and their levels of neutral equilibrium will rise above those of unmixed parcels. Consequently, the cirrus anvils formed by the sinking and spreading of the air in tropical convective plumes may have their upper surfaces in the stratosphere. Danielsen (1982b) proposed an intriguing hypothesis for stratospheric dehydration which depends on the radiative, dynamical, and microphysical processes that occur in anvil clouds. Danielsen pointed out that there will be rapid radiative cooling to space from the top surface of a cirrus anvil, while if there is little cloudiness between the lower surface and the ground, the lower surface should be radiatively heated. Thus, radiation will tend to produce a moist adiabatic lapse rate within the cloud. In this model the radiative cooling at cloud top is balanced by turbulent transport of heat upward within the cloud. Danielsen showed that the vertical temperature flux within the cloud layer necessary to balance a 10 K/day cooling rate from the cloud top was only 5 Kcm/s. However, the large difference in saturation vapor pressure between the bottom and the top of the cloud implies a strong upward flux of water vapor, which would lead to supersaturation and rapid ice crystal growth near the top of the cloud with subsequent fallout of precipitation. Thus, this thermally driven, in-cloud circulation should produce upward heat and vapor fluxes and a downward flux of ice crystals. Danielsen (1982b) argued that the net effect should be to dehydrate the radiatively cooled air near the top of the cloud. Therefore, the net effect of tropical convection, when averaged over the entire life cycle of a tropical convective system, should be to transfer very dry air into the stratosphere.

Danielsen's dehydration hypothesis can only be tested by a carefully designed program of in situ measurements with research aircraft. Plans for such experiments are currently being developed at the NASA Ames Research Center. In the meantime it is at least possible to confirm that currently available evidence is consistent with a model in which cirrus anvil clouds play a major role.

RADIATION BUDGET AND CLIMATE EFFECTS

The potential effects of perturbations in ozone and other trace species on the temperature in the atmosphere and at the ground (i.e., on the climate) has recently been analyzed in WMO (1982c). Thus, only a brief summary of current thinking is given here. The climatic effects of trace species occur in the form of both direct radiative effects involving radiatively active trace gases and indirect effects involving very complex interactions among radiative, photochemical, and meteorological processes. The former class of effects can be calculated in a rather straightforward manner; the latter, however, often depends not just in magnitude, but even in sign, on poorly understood aspects of the climate system such as cloud-radiation feedbacks. Thus, many of the possible climate perturbation scenarios currently are somewhat speculative in nature.

Several of the anthropogenically produced minor trace species (e.g., methane and the CFCs) have strong absorption lines in the infrared region to which the atmosphere is otherwise transparent. Thus, methane and CFCs in the atmosphere contribute to the "greenhouse" effect of carbon dioxide and water vapor in the troposphere. Estimates in WMO (1982c) suggest that if current trends continue, these minor gases could by their direct radiative effects produce a surface warming comparable to that expected from the predicted increase in carbon dioxide.

However, the effect on the surface radiation budget is only a small aspect of the total radiation-climate problem. Models predict that surface temperature rises due to increasing carbon dioxide will be accompanied by temperature decreases in the stratosphere. Because of the temperature dependence of chemical reactions in the ozone layer, this cooling should lead to a moderation in the reduction expected from increased concentrations of minor species. Thus, the ozone perturbation problem can not really be decoupled from the carbon dioxide problem. This type of radiative-photochemical interaction is further complicated by the fact that the temperature structure is tightly coupled to the dynamics, so that changes in circulation would accompany any radiatively induced temperature change, and the change in circulation might influence the transport of ozone. No models currently in existence are able to treat all of these interactions properly.

Perhaps the most challenging aspect of the problem of climate perturbation is the role of water vapor. As pointed out earlier, the extreme aridity of the stratosphere is still not completely understood, although it seems clear that some sort of "freeze-drying" process must occur as air enters the stratosphere through the tropical tropopause. Simple models suggest that increases in carbon dioxide would reduce the temperature at the tropical tropopause, and hence would be expected to reduce the mean water vapor mixing ratio in the stratosphere. On the other hand, any climatic change that resulted in a warmer tropical tropopause could lead to a large increase in stratospheric water vapor. Because water vapor is radiatively active and plays a significant role in the hydroxyl chemistry, a significant increase in stratospheric water vapor could have profound effects. However, a better physical understanding of the processes that maintain the tropical tropopause appears to be required before the plausibilty of a scenario involving warming of the tropopause can be adequately assessed.

RESEARCH RECOMMENDATIONS

- Variability. The large interannual variability observed in the stratosphere poses a significant barrier to the analysis of trends in ozone and temperature. To deduce the nature of the spectrum of natural variability and to define a stable climatology, a long-term commitment to routine global measurements of temperature and ozone is recommended. The SBUV instrument, which is planned for operational flight on the NOAA satellites, should provide adequate monitoring of total ozone and the profile above the level of peak concentration. However, there are no plans for routine satellite observation of the ozone profile in the lower stratosphere where transport processes are crucial to maintaining the ozone budget. Infrared limb scanning appears to be the best available technique for the lower stratosphere, but there are no plans for long-term observations by this method.

Current plans for measuring temperature are totally inadequate for developing a proper stratospheric climatology. The only operational satellite sounder with stratospheric channels is the SSU. However, the SSU may not be flown on operational satellites after the middle of this decade. In any case the SSU provides very little information near the stratopause where ozone perturbations might first be inferred from observed temperature variations if accurate temperature monitoring were available. Further, the SSU temperatures are determined not by inverting the radiances, but by regression against "ground truth" provided by rocket temperature profiles. With the decline in the frequency of meteorological rocket launches, it will be increasingly difficult to provide suitable calibration for the SSU. Steps should be taken as soon as possible to provide for long-term measurement of temperature and ozone for the global stratosphere.

- Stratosphere-troposphere exchange. There is a pressing need to understand the mechanism and spatial and temporal distribution of exchange in the tropical regions in order to account properly for the observed water vapor distribution in the stratosphere. A solution of this problem will require, at the very least, one or more carefully designed aircraft-based experiments with instrumentation capable of defining the details of the dynamical, radiative, and microphysical processes.
- Small-scale waves and turbulence. To improve the current, generally unsatisfactory simulations of the winter stratosphere in three-dimensional general circulation models, efforts must be made to determine the role of small-scale gravity waves and turbulence in the momentum budget of the stratosphere. Unless the problem of the overly cold polar winter stratosphere that is common to most simulations is solved, it will be difficult to use the models for ozone perturbation and other climate perturbation studies. To understand the perturbed climate, we must understand the natural climate first!
- The lower stratosphere. Efforts to evaluate the effects of transport and variability on the ozone budget of the lower stratosphere must be increased. In light of the importance of this region in compensating for calculated ozone decreases in the photochemically controlled upper stratosphere, a quantitative understanding of the interaction of transport and chemistry in the lower stratosphere should be given very high priority.

Unfortunately, definitive studies of this region will require very sophisticated three-dimensional models. Current models are only beginning to be able to provide adequate simulation of the current climate, and several years of effort will be required to develop credible coupled dynamical-radiative-photochemical simulation models. However, in the interim more work should be done with simplified models to test the sensitivity of chemical processes to transport. The study of the winter polar distribution of odd-nitrogen species by Solomon and Garcia (1983a) is an excellent example of what can be done with simple models.

5

Comparison of Models and Measurements

Chemical modeling of the atmosphere focuses both on the interpretation of current conditions and on the prediction of responses to future changes in atmospheric composition. This chapter compares model calculations with currently available atmospheric data. A thorough understanding of the physics and chemistry of the current atmosphere is a prerequisite to forecasting the state of the atmosphere in the face of known and potential perturbations in the future. The application of chemical models includes the simulation of observed distributions of trace gases, the calculation of chemical lifetimes, the inference of source strengths, and the interpretation of a set of measurements in a global context. In the next chapter, we review model calculations of future trends in atmospheric composition, most notably, ozone concentrations. Since this report is an update, it emphasizes the most recent advances in our understanding of the stratosphere; for a complete presentation the reader is referred to the two recent compendia (NRC 1982, WMO 1982a).

CAPABILITIES OF CURRENT PHOTOCHEMICAL MODELS

The fundamental continuity equation in photochemical modeling may be expressed in terms of the time-dependent change in concentration (n) of species (i),

$$\partial n(i)/\partial t = P - L + FD$$

where P and L are production and loss rates by chemical processes, respectively, and FD stands for the divergence of the flux. In this simplified form the chemical term

(P - L) is generally nonlinear, depending on sunlight, temperature, pressure, and the concentrations of many other trace species. The dynamical term FD involves only species (i), but is inherently multidimensional. A highly resolved "wind" field is required to determine the flux of (i) in three dimensions. The current diversity in chemical-dynamical models of the stratosphere reflects, in part, the range of compromises made in treating the chemistry and dynamics in this equation so that the computational effort is feasible.

One-dimensional Models

Photochemical models that abbreviate the order of the dynamical term to only one dimension are able to simulate the most complex chemical reaction schemes yet proposed for the stratosphere. Such calculations involve the simultaneous, coupled chemical interactions of more than 30 species, as well as a detailed description of the solar radiation field from dawn to dusk. Recent reviews (Baulch et al. 1982, WMO 1982a) have helped to promulgate a standard set of reactions, reaction rates, solar fluxes, and cross sections for use in photochemical models. The treatment of solar flux in the complex Schumann-Runge band system of molecular oxygen has received attention recently (Frederick and Hudson, 1980) and thus has become one of the more standard components among the different models. Radiative-transfer calculations including scattered light are standard in most of these models. Several models now simulate the effects of a spherical atmosphere at dawn and dusk, as well as including the effects of diurnal variations in ozone upon the local, ultraviolet field (e.g., Prather 1981).

A severe limitation of the one-dimensional (1-D) models lies in their coarse approximation of transport. The flux divergence term in the continuity equation is effectively averaged over latitude and longitude and then approximated by "eddy"-diffusive transport in the vertical direction. The diffusion coefficients are derived from calibrating the 1-D model against the observed stratospheric profiles of several trace gases (Massie and Hunten 1981) and are then applied equally to all trace gases. The established 1-D chemical model is still popular because it works--providing a good simulation of the vertical distribution of trace gases especially at northern midlatitudes--despite the apparent problems: for example, the latitudinal averaging must span the wide range in photochemical activity from equator to pole, direct advective transport is not included, and the stratosphere clearly shows, at a minimum, two-dimensional structure.

One-dimensional models with detailed photochemistry have been used in a multidimensional mode by approximating latitudinal mixing in the stratosphere as a rapid process that occurs preferentially along mixing surfaces (Wofsy 1978). An adjunct to one-dimensional models is the recent study by Solomon and Garcia (1983b) in which the chemical evolution of an air parcel is followed as it moves through the winter stratosphere. These studies take advantage of specific geometry or atmospheric conditions, but do not calculate the transport of trace species in more than one dimension.

Two-dimensional Models

Two-dimensional (2-D) models of the stratosphere are at least capable of simulating the large variations observed with latitude and season. Traditionally these models average the continuity equation longitudinally, portraying the stratospheric circulation in the latitude-altitude plane. Transport processes include advection by the mean meridional circulation, yet still retain significant diffusion, which is meant to account for zonal averages over longitudinally asymmetric winds. Early 2-D models employed simplified chemical schemes with reduced numbers of species and no diurnal variations in sunlight. Recently these models have incorporated photochemical mechanisms as complete and accurate as their 1-D counterparts (Miller et al. 1981, Fabian et al. 1982, Ko et al. 1983, Solomon and Garcia 1983a, Whitten et al. 1983). They have been used with moderate success to simulate current stratospheric distributions of ozone, nitrous oxide, and chlorofluorocarbons (Ko and Sze 1982, Owens et al. 1982b), as well as to calculate perturbations to ozone (Borucki et al. 1980, Haigh and Pyle 1982, Steed et al. 1982, Whitten et al. 1983). The 2-D and 1-D models do not predict significantly different distributions of long-lived trace gases such as CFCs, N_2O, and CH_4, but the 2-D simulations are able to examine the coupled variations of ozone with latitude and season. Recent research on Lagrangian transport (i.e., following the center of mass of a parcel of air) in the stratosphere

(Andrews and McIntyre 1978, Dunkerton 1978) has led to entirely new approaches to calculating effective tracer transport in the stratosphere (Holton 1982a, Tung 1982). While these methods have not yet been implemented with full chemical-reaction schemes, they should significantly improve the accuracy of 2-D calculations and clarify our understanding of transport mechanisms in the stratosphere.

Three-dimensional Models

In three-dimensional (3-D) models of the stratosphere, the dynamical term in the continuity equation need be averaged over only small space and time intervals. Transport of trace species occurs through direct advection by the three-dimensional wind fields, and the approximation of eddy diffusion (necessary to the 1-D and 2-D models) is no longer the dominant mechanism of transport. All of the current 3-D models for atmospheric transport of trace gases are linked intimately to a parent general circulation model (GCM) (Mahlman et al. 1980, Golombek 1982, Fung et al. 1983). It is difficult to imagine deriving the necessarily detailed and self-consistent wind fields needed for a three-dimensional tracer transport without a general circulation model.

The complexity and scale of 3-D models make it difficult to include a realistic chemical-reaction scheme. For example, even models with the coarsest resolution require in excess of 10 million complete photochemical calculations per model year (e.g., more than one year of time on a VAX 11/780 computer for the chemistry alone). Thus, most experiments with these models are limited to linear loss rates, often unassociated with chemistry. The pioneering study by Mahlman et al. (1980) examined the transport of an ozonelike tracer with a fixed mixing ratio at the upper boundary and a loss due to "rainout" in the troposphere. Similarly, the recent 3-D studies of the effects of planetary waves on chemistry (Rood and Schoeberl 1983) employed a linear approximation to stratospheric chemistry in which chemical reactions were not directly included. The application of chemistry to a 3-D model is currently limited to losses of a trace gas that are linearly proportional to its concentration and that are fixed, independent of the local chemistry involving these trace gases. Some examples include studies of nitrous oxide (Levy et al. 1979, 1982) and CFCs (Golombek 1982). Three-dimensional models are able to simulate the zonal asymmetries in trace gases and hence are essential to interpreting the temporal and spatial variability observed in global measurements (see Chapter 3).

Future Developments

Further advances in the art of photochemical modeling of the stratosphere will come about only through more intimate coupling of the chemical and dynamical processes. The new generation of 2-D models with fully coupled, nonlinear chemistry is just now available; validation and intercomparison of these models seem possible within the next several years. Efforts to put chemistry into a GCM represent the most important long-range goal for research. Such a combination is necessary to make accurate predictions of ozone perturbations, in which a chemical change in ozone alters the solar heating of the stratosphere, which perturbs the stratospheric circulation, which in turn affects the supply of trace gases (N_2O, CH_4, CFCs) to the chemically active regions.

Despite this great need for development of more complex stratospheric models, the importance of the 1-D model must not be overlooked. These models are well developed, are the mainstay of most theoretical work, and provide direct insight into the local chemical processes within the stratosphere.

TRENDS IN ATMOSPHERIC HALOCARBONS AND OTHER TRACE GASES

Increases in the atmospheric abundances of several chlorofluorocarbons as well as other trace gases have been documented in the past few years. The slow increase in N_2O concentrations (0.2 percent per year) (Weiss 1981) has recently been confirmed (Prinn et al. 1983a) and seems likely to be associated with human activities in one way or another (Weiss and Craig 1976, McElroy et al. 1977). Similarly the concentration of methane in the atmosphere is maintained in part by human activities (Ehhalt and Schmidt 1978) and has been observed to be increasing at a rate between 1 and 2 percent per year (Blake et al. 1982, Craig and Chou 1982, Ehhalt et al. 1984, Khalil and Rasmussen 1983b). These trends would most certainly perturb the stratosphere if the trends continued into the next century. Such coupled perturbations are discussed in the next chapter. Here we focus on sources of chlorine in the stratosphere and on the ability of models to predict the rate of increase and global distribution of CFC-11 ($CFCl_3$), CFC-12 (CF_2Cl_2), CFC-22 (CHF_2Cl), CCl_4 (carbon tetrachloride), and 1,1,1-trichloroethane (CH_3CCl_3, methylchloroform) at assumed release rates. The long-range goal in these investigations is the prediction of the amount of chlorinated species in the atmosphere at some time in the future based on assumptions about release rates. The stratospheric concentration of a given trace gas will be proportional to its rate of release multiplied by its atmospheric lifetime. Most models show that stratospheric ozone will decrease as the concentrations of CFCs and methylchloroform increase (see Chapter 6).

The atmospheric abundance of CFC-11 has been monitored on a more or less regular basis since 1970 (Lovelock 1971). During this period the average concentration in the Northern Hemisphere has increased from about 40 to more than 200 ppt. We may define the atmospheric lifetime of a gas as the ratio of its global abundance to its globally integrated loss rate. The atmospheric lifetime of CFC-11 is significantly long compared with its rapidly increased use over the past two decades, so that its concentration is not yet in a steady state (in which releases to the atmosphere are balanced by total, global losses). Approximately 90 percent of all CFC-11 produced has been released to the atmosphere (Chemical Manufacturers Association 1983) and about 90 percent of this amount remains in the atmosphere today. The largest sources of this man-made gas are associated with the industrial countries of the northern midlatitudes, and its tropospheric distribution shows the expected latitudinal gradient. Significant effort has gone into compiling statistics on its rate of release (Bauer 1979, Chemical Manufacturers Association 1983). See Figure 5-1.

Recent reports have examined time series of self-consistent measurements of CFC-11. Brice et al. (1982) report on data taken at Harwell, U.K., during the period 1975-1981 and derive a best estimate for CFC-11 lifetime of 75 years. Fraser et al. (1983) calculate a similar lifetime based mainly on 1976-1980 data from Cape Grim, Tasmania. Singh et al. (1983) report a lifetime of 60 years with a range of 40 to 100 years. The Atmospheric Lifetime Experiment (ALE) (Prinn et al. 1983) set up stations in Ireland, Oregon, Barbados, Samoa, and Tasmania for the continuous monitoring of CFC-11, CFC-12, CCl_4, CH_3CCl_3, and N_2O. Based on the data from July 1978 to

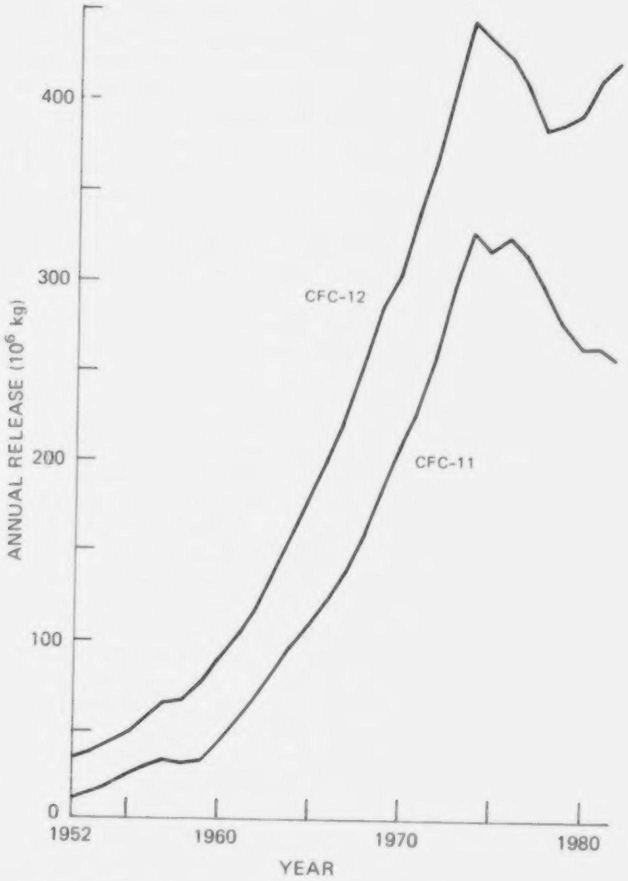

FIGURE 5-1 Estimated annual worldwide releases of CFC-11 and CFC-12, 1952-1980. SOURCE: Chemical Manufacturers Association (1983).

June 1981, the best ALE estimate for CFC-11 lifetime is 78 years with a 90 percent certainty range of about 50 to 150 years. Most of the previous analyses, based mainly on data from a single station, rely on 2-D models to simulate the latitudinal distribution of CFC-11 near the surface. From the relative precision of the ALE data and its distribution of stations, one is better able to infer the global content of CFC-11 and can make a second, independent estimate of the atmospheric lifetime from the trends in release of CFC-11 and the observed trends at each station. These lifetimes--based on estimates for release and on observational data--are consistent with 2-D models in which photolytic decomposition in the stratosphere is the only loss of CFC-11 (Ko and Sze 1982, Owens et al. 1982b). In calculations assuming that the release of CFC-11 continues at the current rate, steady-state concentrations on the order of 1 ppb are reached in the next hundred years (Owens et al. 1982b), and the concentration of stratospheric chlorine increases by as much as 3 ppb.

The situation for CFC-12 is similar to that for CFC-11 except that fewer observational data are available. Theoretical 2-D calculations with only stratospheric losses for CFC-12 predict lifetimes in the range from 120 to 140 years (Ko and Sze 1982, Owens et al. 1982b). Application of the newly proposed cross sections for molecular oxygen (see Chapter 2) indicates somewhat shorter lifetimes for CFC-12, 115 years, and also for CFC-11, 56 years (Ko and Sze 1983). The ALE data for CFC-12 is consistent with lifetimes greater than 100 years, but it is difficult to detect such small losses over the length of observation (Cunnold et al. 1983a,b). Similar results are reported by Singh et al. (1983) from independent data. In calculations assuming that CFC-12 releases remain constant at today's rate, a steady-state concentration of approximately 2.5 ppb is eventually reached (Owens et al. 1982b), and CFC-12 then contributes an additional 5 ppb of chlorine to the stratosphere.

Considerable disagreement with regard to the observed growth rate of CFCs and published estimates of their release rates (Jesson 1980, Chemical Manufacturers Association 1983) has recently arisen. Rowland et al. (1982) examined a series of measurements made from 1976 through 1980 and derived a release pattern for CFC-12 that indicated a substantial underestimate of the released gas by an earlier Chemical Manufacturers Assocation (CMA) report. The use of a larger observational data set and, to a lesser extent, a minor revision of the CMA release history for CFC-12 due to an expanded source from Eastern Europe, appear to resolve the discrepancy. Similar analysis of CFC-11 at Tasmania has led Fraser et al. (1983) to recalculate a release scenario from 1974 to the present. Considerable uncertainty must be associated with all of these results, which rely heavily on the absolute calibration and instrumental accuracy of early measurements of CFCs.

The CFCs have well-resolved release patterns for anthropogenic gases and thus provide an excellent test of atmospheric transport (e.g., Lovelock 1971). Two recent modeling efforts have examined CFCs in three-dimensional tracer models based on GCMs (Golombek 1982). The concentrations of CFCs, as measured near the surface of the Earth, are expected to have significant zonal asymmetry, especially in the Northern Hemisphere (Figure 5-2). Model calculations and observed ALE trends are shown in Figures 5-3 and 5-4 for two of the ALE stations, Ireland and Samoa. The currently accepted release rates, the ALE data, and the theoretical models taken together produce a consistent picture of the growth of CFC-11 and CFC-12 during the past five years.

CFC-22, CHF_2Cl, is observed to be increasing rapidly and may represent a significant source of chlorine to the stratosphere in the future (Fabian et al. 1981). CFC-22 is destroyed mostly in the troposphere by reaction with hydroxyl radical and has a lifetime of about 16 years (based on Logan et al. 1981). The 1977 release rate (Jesson 1980) would contribute, in steady state, only 0.1 ppb chlorine to the atmosphere. The production and release of CFC-22 would have to increase at least 20-fold if it is to be an important perturbation to the stratosphere.

Methylchloroform (CH_3CCl_3) is an industrially produced chlorocarbon with a well-documented rate of increase in the atmosphere, 9 percent per year (Prinn et al. 1983b, Singh et al. 1983). The Atmospheric Lifetime Experiment (Prinn et al. 1983b) infers a lifetime of 10 years based on available release data. This value may be as small as 6.5 years, however, if the time delay between the known industrial production and release is increased. This range in lifetimes is consistent with model calculations in which the dominant loss is through reaction with hydroxyl radicals in the troposphere (Logan et al. 1981, Volz et al. 1981). Currently, methylchloroform contributes approximately 0.3 ppb chlorine to the stratosphere. In order to cause significant future perturbations to the stratosphere, the production and release of methylchloroform, as of CFC-22, would have to continue to increase.

Carbon tetrachloride (CCl_4) is currently an important chlorinated species in the atmosphere, contributing approximately 0.5 ppb chlorine to the stratosphere (Brice et al. 1982). The ALE analysis (Simmonds et al. 1983) indicates a lifetime of about 50 years, consistent with most models, and would predict a steady-state abundance

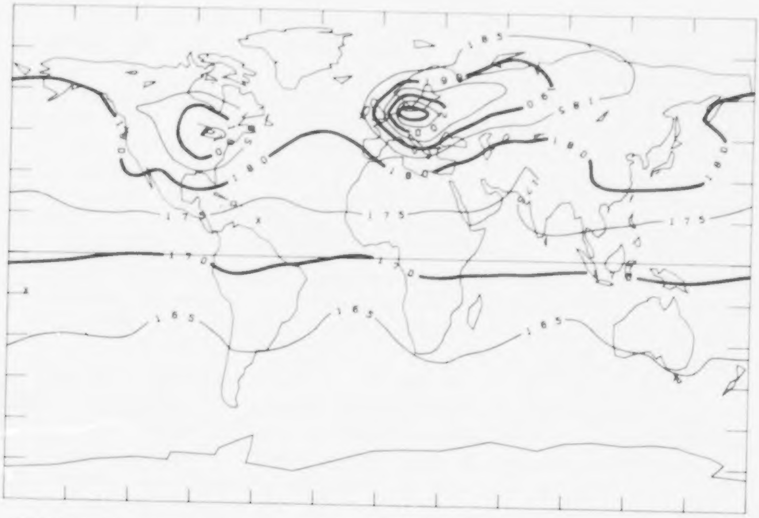

FIGURE 5-2 Calculated global distribution of the average concentration of CFC-11 at the Earth's surface in January 1981 (ppt). Results are from Harvard/GISS 3-D tracer model run for this report.

corresponding to about 1 ppb of atmospheric chlorine. Methyl chloride (CH_3Cl), with tropospheric concentrations of about 0.7 ppb (Penkett et al. 1980), has not been discussed since it is probably of natural origin and changes in its atmospheric abundance have not been documented. Table 5-1 summarizes current understanding of the stratospheric concentrations, trends, lifetimes, and calculated steady-state contributions of chlorine to the stratosphere by the major source gases of chlorine in the stratosphere.

STRATOSPHERIC DISTRIBUTION OF LONG-LIVED TRACE GASES

An important, classical test of stratospheric models has always been comparison of calculated values with the vertical profiles of long-lived trace gases in the stratosphere (e.g., NRC 1982, WMO 1982a). Observations of N_2O, CH_4, CFCs, other halocarbons, and other hydrocarbons from several balloon flights in the northern midlatitudes, or less often in the tropics, are collected and plotted as data points for comparison with the continuous curves

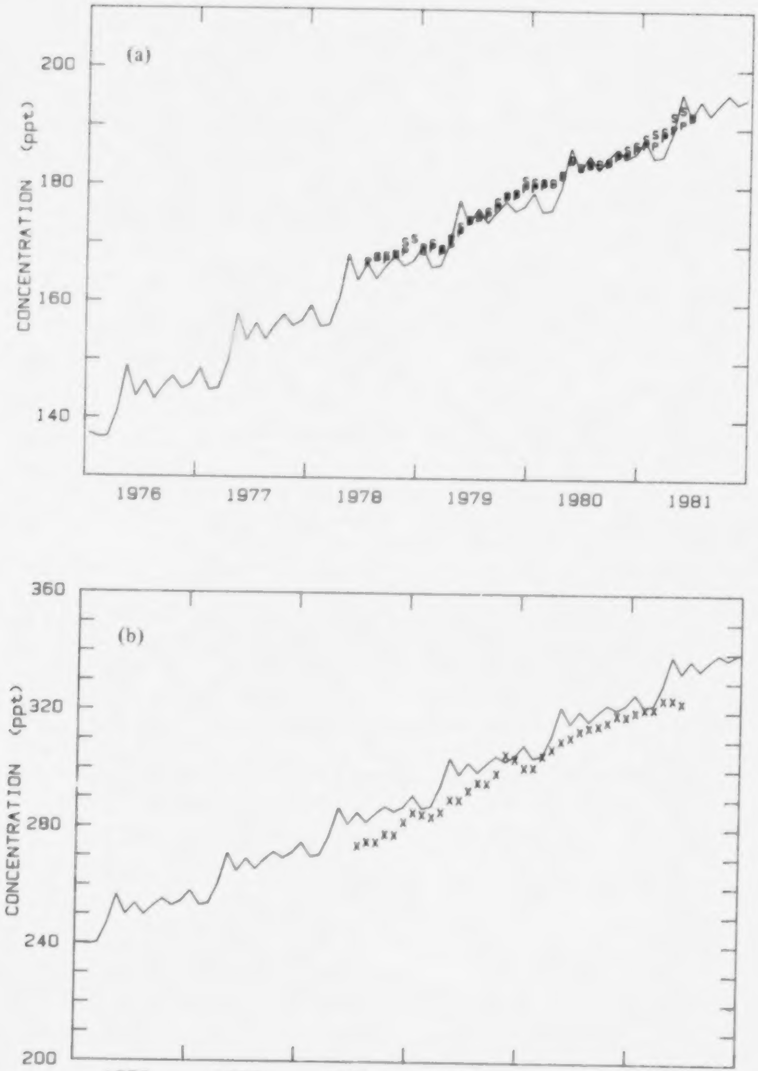

FIGURE 5-3 Observed and calculated trends in monthly mean concentrations of (a) CFC-11 and (b) CFC-12 at ALE station in Ireland, 1976-1981. Calculations are from Harvard/GISS 3-D tracer model run for this report; data are indicated by S, P, and X. SOURCE: Data from Cunnold et al. (1983a,b).

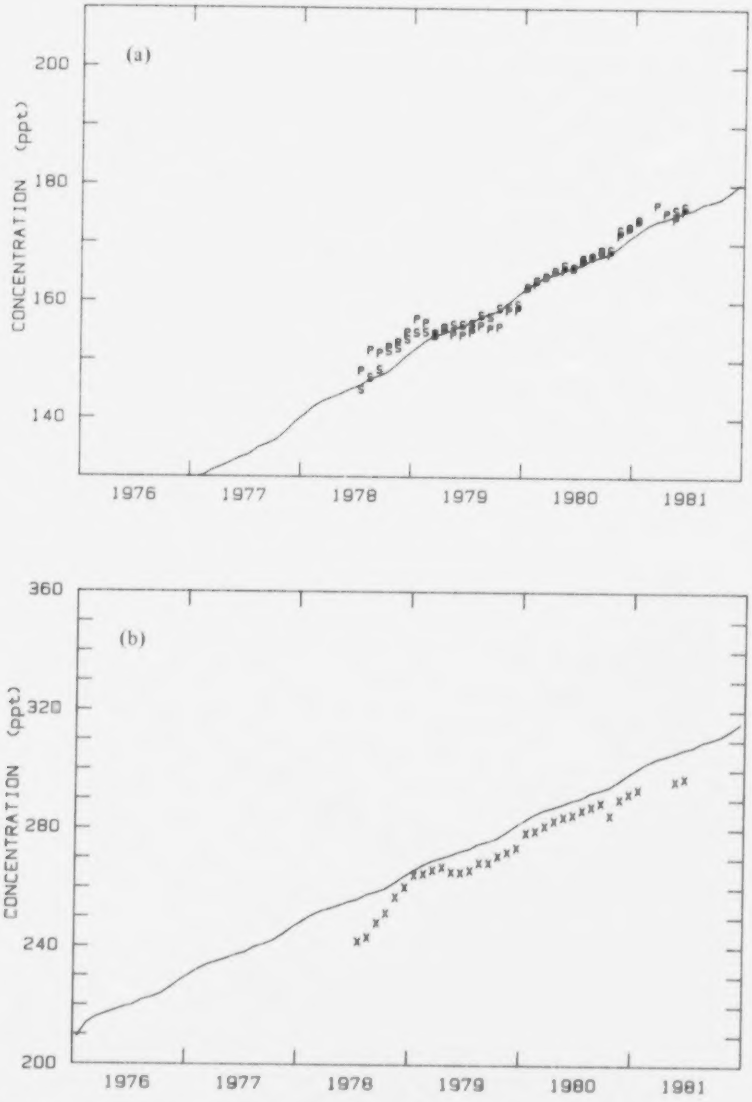

FIGURE 5-4 Observed and calculated trends in monthly mean concentrations of (a) CFC-11 and (b) CFC-12 at ALE station in Samoa, 1976-1981. Calculations are from Harvard/GISS 3-D tracer model run for this report; data are indicated by S, P, and X. SOURCE: Data from Cunnold et al. (1983a,b).

TABLE 5-1 Chlorinated Gases in the Stratosphere Circa 1980

Source Gas	Concentration (ppb total Cl)	Rate of Increase of Tropospheric Abundance (%/year)	Atmospheric Lifetime (year)	Steady-state, Based on Current Releases (ppb total Cl)
$CFCl_3$ (CFC-11)	0.5	6	65	2.0
CF_2Cl_2 (CFC-12)	0.5	6	120	5.0
CHF_2Cl (CFC-22)	0.05	>6 ?	16	>0.05[a]
CH_3CCl_3	0.3	9	6.5	>0.3[a]
CCl_4	0.5	2	50	1.0
CH_3Cl	0.7	0 ?	< 1	0.7

[a] Release rate is uncertain.

obtained from theoretical models. A new, more objective approach to the analysis of observational data has been presented by Ehhalt et al. (1984). The observational data have not changed significantly since the previous reviews (see Chapter 4), but the physics and chemistry of the models continue to evolve (see Chapter 2). New theoretical results for the long-lived trace gases are presented in this section, and for radicals and for ozone in the following two major sections.

New Interpretation of Stratospheric Measurements

A new method of interpreting the variability in stratospheric observations has been developed by Ehhalt et al. (1984). They note that the spread in measured concentrations of N_2O, CH_4, CFC-11, and CFC-12 at a particular altitude in the stratosphere is much greater than the expected instrumental error. This species-dependent variance at a given altitude is equated with an effective displacement in altitude that shows similar behavior for all trace gases. The effective vertical displacement is shown to correspond to an effective latitudinal mixing length across surfaces of constant mixing ratio (e.g., Reed and German 1965). These arguments are supported by the correlation between effective vertical displacements of N_2O and CH_4 in the same air sample. Ehhalt et al. (1984) conclude that the observed variances in stratospheric concentration of several long-lived gases are a combination of instrumental uncertainties and atmospheric variability associated with meridional mixing. A similar investigation using a 3-D general circulation model of the stratosphere is being sponsored jointly by the

Aeronomy Laboratory and Gas Fluid Dynamics Laboratory of NOAA (J.D. Mahlman, Princeton University, personal communication, 1983). When compared with traditional methods of combining observations with theory, these efforts present not only a more objective, but also a more quantitative technique for comparison of stratospheric data with theoretical models (see essay on modeling and tracer transport in WMO 1982a).

Updated Model Calculations

The recent revisions in kinetic rates for odd-hydrogen species and in cross sections for oxygen (see Chapter 2) have produced notable changes in the modeled profiles for some long-lived trace gases (Froidevaux and Yung 1982, Ko and Sze 1983). The major effect is due to the calculated increase in solar radiation in the ultraviolet region at about 200 nm, and also to the computed increase in concentrations of OH radicals in the upper stratosphere. This section presents revised calculations from the Harvard 1-D model; the discussion is based on the original comparison between models and data from the review by Wofsy and Logan in the previous NRC (1982) report. In the current calculations, the cross section for molecular oxygen between 200 and 220 nm was taken as the average of values from Shardanand and Prasad-Rao (1977) and from Herman and Mentall (1982), agreeing with the laboratory measurements of Yoshino et al. (1983).

Calculated methane profiles changed slightly in the models, decreasing by 10 to 25 percent in the stratosphere as calculated concentrations of OH increased with use of the new kinetic rates. The new (1983) model result for methane is compared with the previous (1981) calculation and observational data in Figure 5-5. Considering that most of the observations are made near 45°N, the revised models show a slightly poorer agreement with the methane data. Much larger adjustments have occurred in the modeled profiles for N_2O, $CFCl_3$, and CF_2Cl_2 (Figures 5-6, 5-7, and 5-8, respectively). The increased solar radiation near 200 nm has effectively lowered all of these profiles calculated at 30°N by about 2 km. As noted by Ehhalt et al. (1984), objective evaluation of the accuracy of a photochemical model is difficult given the currently available observational data. Nevertheless, the recent revisions in the photochemistry appear to represent a general improvement in our capability to model the long-lived gases in the stratosphere.

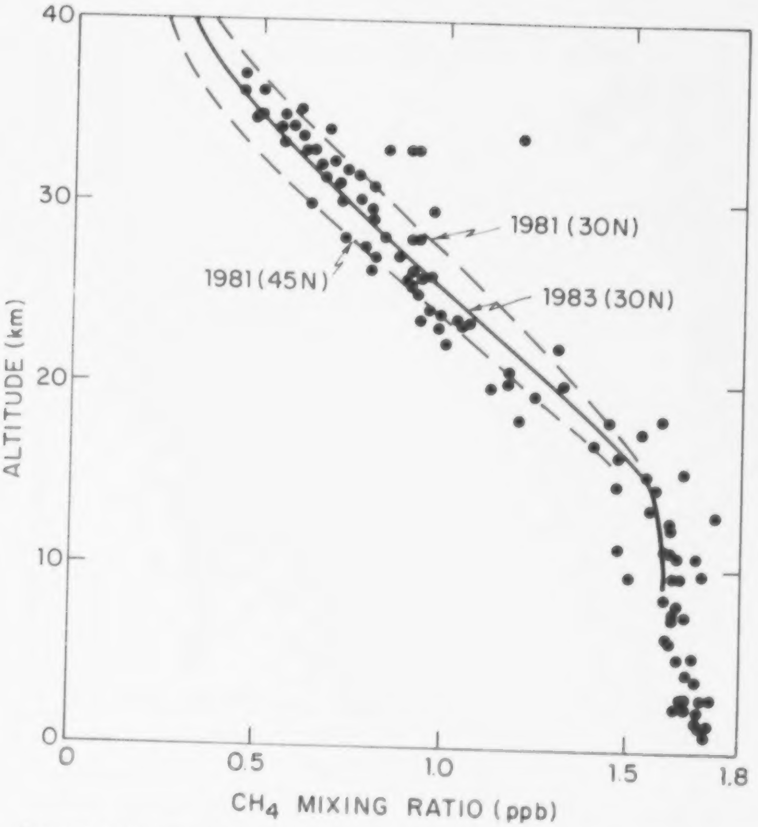

FIGURE 5-5 Comparison of observed stratospheric concentrations of CH_4 with profiles of concentration calculated with Harvard 1-D model. SOURCE: See NRC (1982) for description of data and model.

Water vapor is a special problem in modeling the stratosphere. Its concentration reflects directly on the active chemistry; it is a primary source of hydroxyl radicals. The photochemical production of water by the conversion of methane into carbon monoxide is readily modeled, but the processes that maintain the concentration of water in the lower stratosphere cannot be easily described in current photochemical models. A major measurement program has recently examined the transport of water across the tropical tropopause

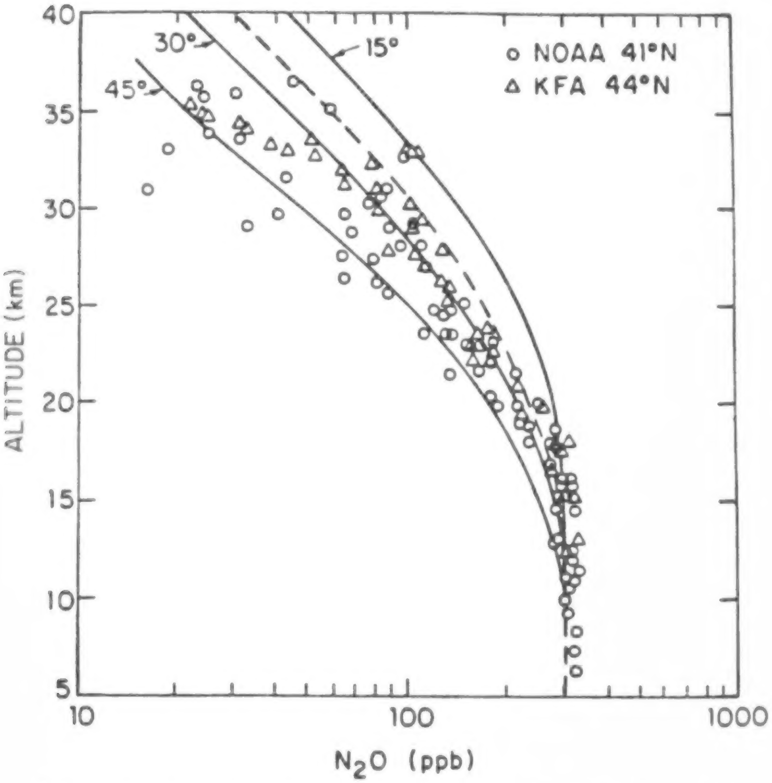

FIGURE 5-6 Comparison of observed stratospheric concentrations of N_2O with profiles of concentrations calculated with Harvard 1-D model. Broken curve is 1981 model result for 30° north latitude, and solid curves are current (1983) results. SOURCE: See NRC (1982) for description of data and model.

(Danielsen 1982b, Kley et al. 1982, Knollenberg et al. 1982). The overall results are inconclusive or contradictory (Ellsaesser 1983), but they point to the importance of small-scale, perhaps cloud-related heterogeneous sinks for water vapor in the lower stratosphere. Understanding these "microphysical" processes controlling the abundance of water in the stratosphere is essential. Changes in water associated possibly with volcanic activity or with altered stratospheric temperatures would have a direct and significant impact on stratospheric ozone.

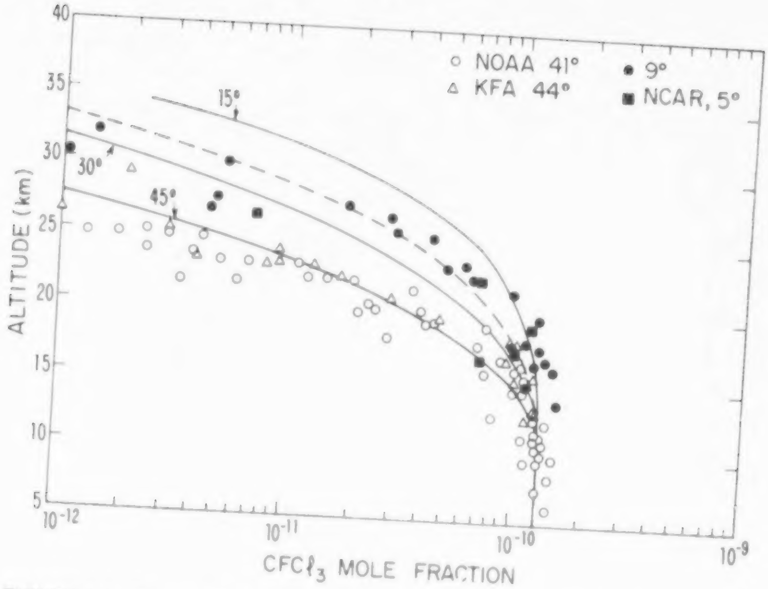

FIGURE 5-7 Comparison of observed stratospheric concentrations of $CFCl_3$ with profiles calculated with Harvard 1-D model. Broken curve is 1981 result for 30° north latitude, and solid curves are current (1983) results. SOURCE: See NRC (1982) for description of data and model.

CHEMICALLY ACTIVE SPECIES IN STRATOSPHERIC MODELS AND MEASUREMENTS

Highly reactive chemical species, such as O, OH, HO_2, NO, NO_2, Cl, and ClO, play a direct role in the chemistry of ozone in the stratosphere, participating in rapid, catalytic sequences of reactions that destroy ozone (see NRC 1982, WMO 1982a, Bower and Ward 1982, for a complete review). Since these reviews, new observations have become available and new theoretical interpretations have come to light. We focus first on NO_x in the stratosphere and then on the overall effects of the revised chemistry (Chapter 2) on calculated distributions of radicals.

New Data and Theoretical Interpretations

An important example of innovative coupling of theoretical research and observations in the past two years has been

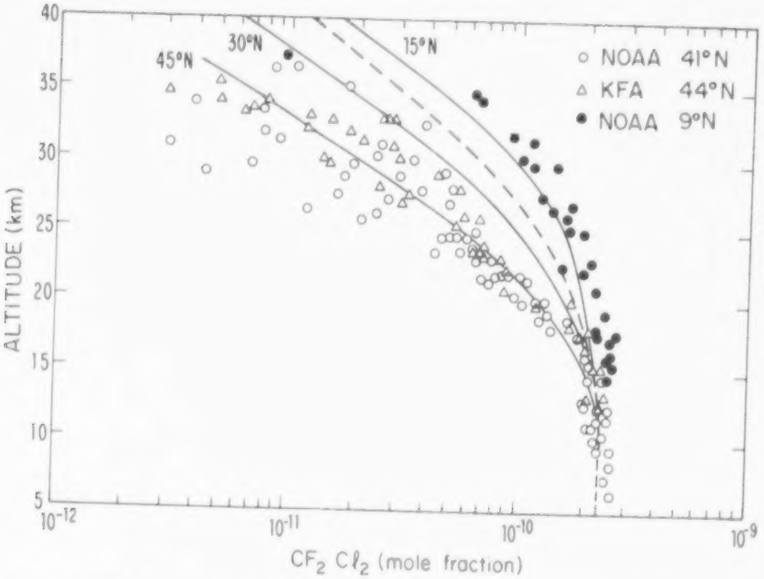

FIGURE 5-8 Comparison of observed stratospheric concentrations of CF_2Cl_2 with profiles calculated with Harvard 1-D model. Broken curve is 1981 result for 30° north latitude, and solid curves are current (1983) results. SOURCE: See NRC (1982) for description of data and model.

the study of NO_x chemistry in the stratosphere. Original observations by Noxon (1975) showed unusual behavior for NO_2 near the winter pole. The Noxon "cliff," in which NO_2 almost disappears from the polar air, has spawned intensive research into the partitioning among members of the NO_x family. Tentative observations now available for N_2O_5 (Roscoe 1982) agree reasonably with theoretical models (see Figure 18 of Solomon and Garcia 1983a). More detailed measurements of NO_3 (Rigaud et al. 1983) similarly show qualitative agreement with models (Figure 5-9). An extensive new data set for NO_2 from the SME satellite (see Chapter 3) has confirmed Noxon's ground-based measurements. It shows that air with low NO_2 is intimately associated with a closed flow about the pole and that most of the air within this polar vortex, which experiences a long winter night, is deficient in NO_2.

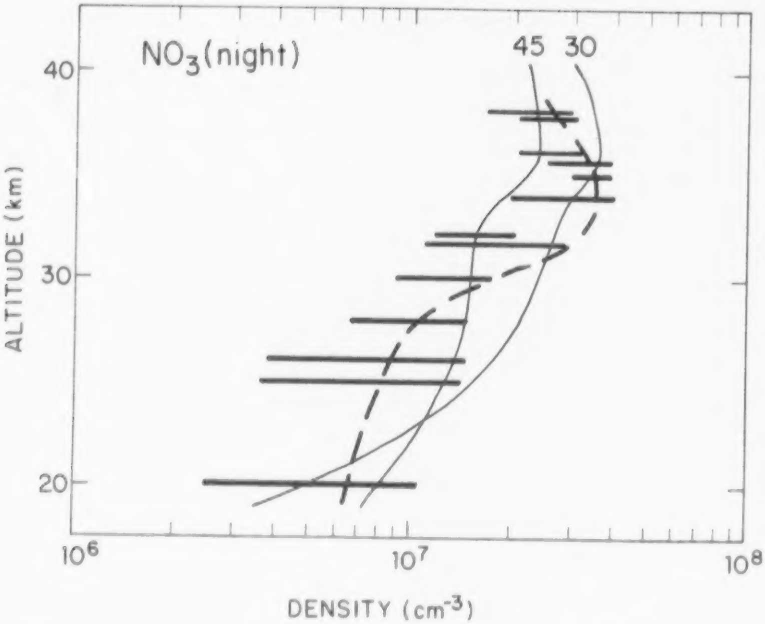

FIGURE 5-9 Comparison of observed concentrations of NO_3 with profiles calculated with Harvard 1-D model. SOURCE: Data from Rigaud et al. (1983).

Recent theoretical answers to the question of the missing NO_2 do not represent completely satisfactory solutions. The coexistence of multiple solutions to atmospheric chemistry has been examined in greater detail, including diurnal chemistry (Fox et al. 1982), but the time for conversion of NO_2 into $ClNO_3$ appears to be too long. Solomon and Garcia (1983b) have followed the history of air parcels traveling isobarically in the polar vortex and conclude that most of the NO_2 is converted into N_2O_5. The choice of N_2O_5 as the missing NO_x reservoir is not entirely satisfactory (Noxon et al. 1983); the model of Solomon and Garcia produces an NO_2 cliff of proper magnitude, but predicts much larger differences in NO_2 between morning and evening than are observed (see Figure 4 of Solomon and Garcia 1983b). The resolution of the winter NO_x problem awaits measurement of several other species such as N_2O_5, NO_3, HNO_3, and $ClNO_3$ within the polar vortex.

Revised Chemical Models

Revisions in photochemical models over the past two years have resulted in a 20 to 30 percent reduction in the calculated abundance of all stratospheric odd nitrogen, including the noted lower concentrations of HNO_3 (Froidevaux and Yung 1982). The decrease in NO_x is due to the reduced source from N_2O; more of the nitrous oxide is photolyzing rather than reacting with $O(^1D)$ to produce two NO molecules (i.e., reaction C-31 of NRC [1982]). Calculations with the revised Harvard 1-D model produce concentration profiles of NO, NO_2, and HNO_3 that are almost uniformly smaller by 20 percent than those figures of Wofsy and Logan in NRC (1982). The catalytic destruction of ozone by NO_x is reduced, and ozone densities would increase by up to 10 percent if this was the only effect on ozone (see next section). Given the large spread in observational data for NO_x species, this revision--although substantial in terms of NO_x--cannot be said to produce better or worse models of the NO_x chemical family. However, a generally improved agreement with HNO_3 above 25 km is apparent (see Appendix C of NRC 1982). A clearly mandated requirement of the chemical model is the observationally defined distribution of total NO_x in the middle stratosphere.

The hydroxyl radical is the keystone to stratospheric chemistry: many catalytic cycles rely on OH reactions, some long-lived gases are destroyed by reactions with OH, and partitioning between active and inactive members of the NO_x and chlorine families is directly controlled by OH (see NRC 1982). Calculated concentrations of OH have increased in the upper stratosphere with the relative shift in rate coefficients for the reactions O + OH and O + HO_2 (Ko and Sze 1983). This effect on the profile of OH is shown in Figure 5-10. Observations of OH lack both the necessary accuracy and sufficient spatial and temporal coverage to test the models adequately (see Chapter 3). A sufficient number of measurements of OH are vitally necessary to define the vertical profile and range of OH concentrations accurately throughout the stratosphere. Such a program is presently in progress and will measure OH with a copper vapor laser (J.G. Anderson, Harvard University, personal communication, 1983). Within a year these new observations may provide one of the most stringent tests of photochemical models.

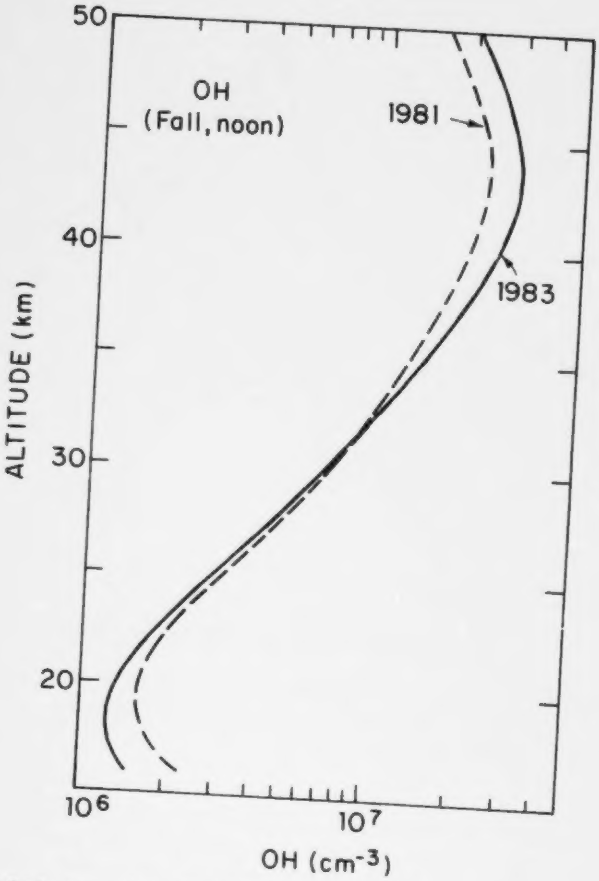

FIGURE 5-10 Comparison of profiles of stratospheric concentrations of OH at middle latitudes in fall using Harvard 1-D model. SOURCE: See NRC (1982) for description of model.

Measurements of the total column of OH provide useful constraints on the chemical models for the upper stratosphere and lower mesosphere where most of the OH resides. Recent observations (Burnett and Burnett 1982) indicate a substantial increase in OH column with solar activity. The increase cannot be attributed directly to changes in solar flux by current theoretical models. Nevertheless, the most recent measurements show a well-

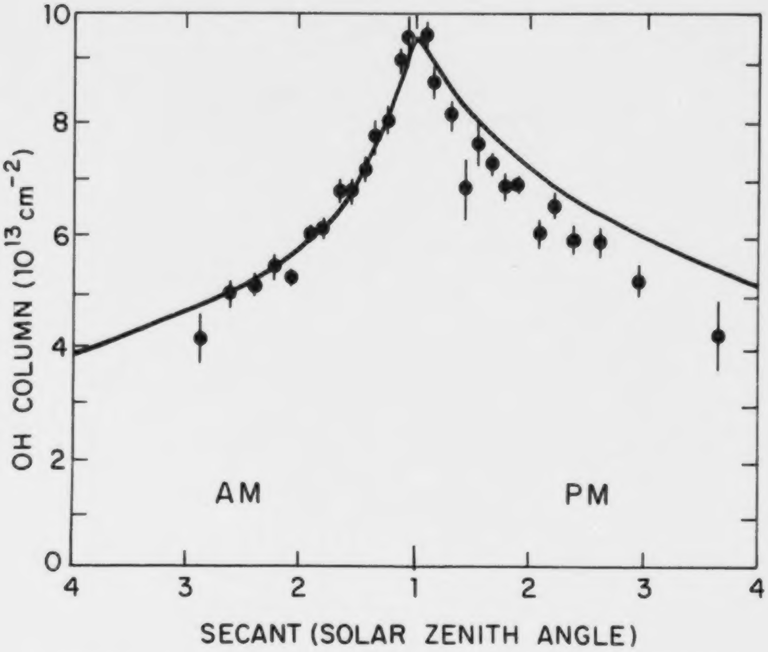

FIGURE 5-11 Comparison of calculated (Harvard 1-D model) and measured values of the total-column density of OH as a function of solar zenith angle. SOURCE: Data from Burnett and Burnett (1982).

defined and asymmetrical behavior of the OH column with solar zenith angle, which is reproduced by models (Figure 5-11). When the most recent kinetic data are used in these models (e.g., Prather 1981), the result is an absolute value for the noontime OH column that is very close to the 1980-1981 values of 9.5×10^{13} cm^{-2} reported by Burnett and Burnett (1982).

The radical ClO has generally received the most attention of all chlorine species. It is the primary reactant in the chlorine catalytic cycle that destroys ozone (see NRC 1982, WMO 1982a). The basic observational data have not changed since the last report (Anderson et al. 1980, Parrish et al. 1981, Waters et al. 1981, Weinstock et al. 1981), but a new measurement (Mumma et al. 1983) has questioned the existence of ClO in the stratosphere below 35 km. Because more recent microwave observations (Solomon et al. 1984) corroborate the measurements of Anderson et al., and the technique of Mumma et al. lacked direct calibration, we assume the values from the traditional measurements in our analysis. This discrepancy must still be resolved, however, before we may place ClO in the category of "fully understood" trace species.

The effects of the revised chemistry on computed concentrations of ClO are shown in Figure 5-12 along with the observational data. The calculations are based on the updated Harvard 1-D model and include a separate profile that considers additionally the revised rate for O + ClO (see Chapter 2). The increased concentration of OH (Figure 5-10) increases the ratio of ClO to HCl. Likewise, the reduced rate for the reaction O + ClO results in higher concentrations of ClO in the upper stratosphere. The cumulative effect of these revisions in the chemical models clearly improves the agreement of models with observations.

The revisions to the chemistry discussed here and in Chapter 2 will have substantial consequences for the calculated perturbations to ozone for different scenarios of the future (see Chapter 6). For example, the reaffirmation of the rate for formation of $ClNO_3$ (Margitan 1983a) makes this species extremely important in the lower stratosphere for scenarios with high chlorine content. The reduced rate for O + ClO will reduce the effects of a chlorine perturbation in the upper stratosphere, but increased OH concentrations produce a higher proportion of total chlorine in the active-phase ClO.

OZONE IN THE STRATOSPHERE

Ozone and its response to stratospheric perturbations are the focus of this report. In this section we describe the rapidly expanding set of data on the global distribution of ozone (climatology). The available data are growing rapidly with the arrival and recent analysis of (mainly pre-1980) data from satellites (Hilsenrath and Schlesinger 1981, Reinsel et al. 1982, Frederick et al. 1983, McPeters et al. 1984; see also the papers on the Solar Mesosphere Explorer in Geophysical Research Letters 10, April 1983). Here we focus on the efforts to discern trends in ozone over the past several decades, and on the ability of the revised photochemical models to calculate the distribution of ozone.

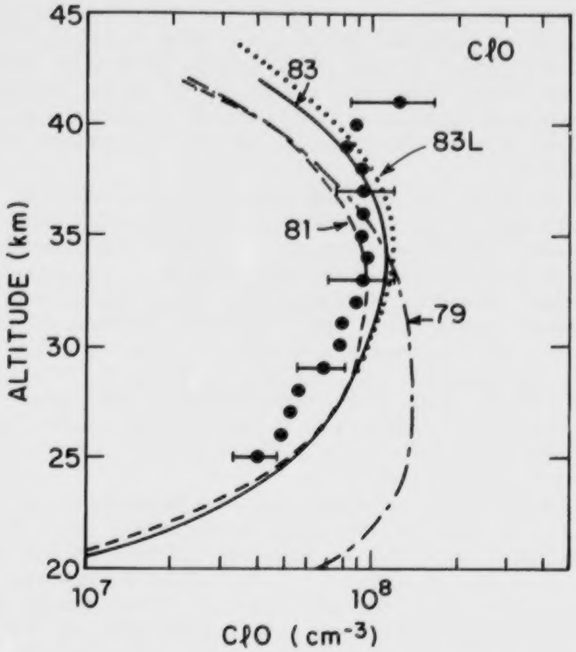

FIGURE 5-12 Comparison of observed concentrations of ClO with profiles calculated with versions of Harvard 1-D model. Calculated values are denoted by year of photochemistry used and refer to a local solar time of about 3:00 P.M. under equinoctial conditions. Dotted curve labeled 83L is result of current model using revised rate for reaction O + ClO → Cl + O_2. Curve labeled 83 indicates chemical model discussed in this report without new O + ClO rate. SOURCE: See NRC (1982) for description of data and model.

Trend Analysis

Clearly there is no better technique for demonstrating the validity of a theory than the direct observation of the predicted effect. Models including only CFC releases have consistently predicted that over the past decade there should have been a decrease in total ozone. Komhyr et al. (1971) were the first to suggest the existence of a decadal increase in the record of total ozone for the Northern Hemisphere during the 1960s. Their findings were confirmed and expanded by others. The early analyses (Johnston et al. 1973; Angell and Korshover

1973, 1976, 1978; Birrer 1974; London and Kelley 1974) were more descriptive than statistical, intending to explore and discover fluctuations in the data. The power of modern statistical techniques for trend detection and hypothesis testing were first introduced by Hill and Sheldon (1975) and Hill et al. (1977), and the ensuing discussions in the scientific community have led to significant advances in analysis of ozone trends and in understanding of the inherent uncertainties or noise associated with the ozone record.

The fundamental concepts for descriptive analysis and statistical time series analysis are summarized in WMO (1982a). Findings based on the earlier techniques are also summarized there. Current advances in ozone trend analysis are based on time series analysis (St. John et al. 1981, 1982; Penner et al. 1982, Reinsel et al. 1982, 1983a,b); or the related frequency-domain technique (Bloomfield et al. 1981, 1982). In general, the analytical model assumes that the monthly averages of total ozone collected at a particular location are made up of four components--the long-term mean value, the annual seasonal variation, the unknown deterministic trend (to be tested), and the noise or the error part. A trend estimate can then be decomposed into global trend, regional trend effect, individual effects for a station within the region, and errors associated with a station.

At least three independent groups have used equivalent techniques on a set of 36 Dobson stations with the longest continuous record covering the period 1960-1979 or 1970-1979. Reinsel et al. (1981) and Bloomfield et al. (1981) tested for a linear trend for the 10-year period 1970-1979, while St. John et al. (1981) tested for a smooth curve similar to the theoretically estimated changes in total ozone due to increases in CFCs only. Respectively, they found the 95 percent confidence intervals for global total ozone trend to be +0.8 ± 1.3 percent, +1.7 ± 2.0 percent, and +1.1 ± 1.2 percent.

More recent analyses have attempted to remove the effects of nuclear testing and possible interventions with the data such as the recalibration shifts at four particular stations. The resulting trends, +0.23 ± 1.24 percent per decade (G. Reinsel and G.C. Tiao, University of Wisconsin, personal communication, 1983) and +0.5 ± 0.4 percent per decade (G. Oehlert, Princeton University, personal communication, 1983), contradict earlier findings that considered only CFC perturbations, but are consistent with theoretical models that include the simultaneous increases in several important trace gases over the decade of the 1970s. The multipollutant scenarios predict an increase in total ozone ranging from 0.1 to 0.4 percent between 1970 and 1980 (see Chapter 6, Sze et al. 1983, Wuebbles et al. 1983, A.J. Owens, Du Pont, personal communication, 1983).

It is now clear that studies of trends in total ozone will fail to provide definitive evaluation of the CFC-ozone depletion hypothesis. We are led naturally to the analysis of the vertical distribution of ozone, since the photochemical theory predicts a more readily detectable change in ozone in the upper stratosphere.

Photochemical model calculations indicate a local ozone decrease in the upper stratosphere during the 1970s that is largely due to CFCs, with a contribution from methane-induced production of H_2O. The maximum local ozone change from 1970 through 1980, calculated using multiple-perturbation scenarios, is about -5 percent and is centered at 40 km (WMO 1982a, D.J. Wuebbles, Lawrence Livermore National Laboratory, personal communication, 1983). Statistical trend analyses similar to those for total ozone have been applied to ground-based Umkehr measurements of the vertical ozone profile. The Umkehr observations are obtained with the same Dobson instruments that measure total ozone, although only 13 of the 36 stations in the Dobson network have a sufficiently complete data base to be useful for trend analysis.

The first statistical trend analyses of the global Umkehr data base indicated an ozone increase (roughly +8 percent) in the upper stratosphere, with large statistical uncertainties (±8 percent) (Bloomfield et al. 1982, D.S. St. John, Petrochemical Department, Experimental Station, Wilmington, Delaware, personal communication, 1983). Reinsel et al. (1983a) identified the existence of several "step changes" in the data at three stations which were primarily responsible for the large positive trends. When these step changes are removed, the upper-stratospheric trends and statistical uncertainty range are substantially reduced to around 0 ± 3 percent. Because the vertical ozone profiles determined using the Umkehr method are sensitive to stratospheric aerosols, Reinsel and co-workers (personal communication, 1983) used the atmospheric transmission observed at Mauna Loa as a proxy variable for the global aerosol effect. They found that with this "aerosol correction" the computed statistical trend for Umkehr layers 6 to 9 (35 to 50 km) is -3 ± 3 percent. Oehlert (1983), using similar methods, obtained similar results. (See also Angell and Korshover 1983.) These analyses show that the Umkehr network is approaching the ability to detect trends in the upper stratosphere of the magnitude calculated by atmospheric models. However, significant questions regarding the global representation of the network (heavily concentrated in the Northern Hemisphere) and the accuracy of basing the aerosol correction on transmission observations from a single station need to be resolved.

A search for trends in the available data from two satellites from 1970 to 1979 (NIMBUS-4 and NIMBUS-7) (D. Heath, Goddard Space Flight Center, personal communication, 1983) has yielded inconclusive results, because the analysis is subject to greater uncertainty due to the lack of intercalibration between the two satellite instruments, the observed--but not well-quantified--instrumental drift, and the necessary corrections for atmospheric aerosols.

Confirmation of a trend of decreasing ozone concentrations in the upper stratosphere on a global scale would help to substantiate the theory of ozone changes associated primarily with releases of CFCs and would present evidence of a substantial alteration of the atmosphere over the entire planet as a result of human activity.

Tropospheric Ozone

Current theory suggests that ozone below the stratosphere, in the upper troposphere, may have been increasing during the past decade or more. Such predictions are based on the photochemical formation of ozone associated with NO_x emitted from high-flying subsonic aircraft. Increases in methane also contribute to the production of ozone through reactions involving tropospheric NO_x.

Angell (in WMO [1982a]) was the first to have reported increasing ozone concentrations in the low-level Umkehr data and from selected ozonesondes, reporting a trend of approximately +0.7 percent per year in the northern midlatitude region around 2 to 8 km in altitude. Reinsel and Tiao (University of Wisconsin, personal communication, 1983) have extended their Umkehr time series analysis and found a +0.95 ± 0.81 percent per year increase for the past decade at altitudes between 5 and 10 km. Similar results are reported in Angell and Korshover (1983). These results are also applicable to northern midlatitude regions where data exist, and are consistent with some model calculations of +7 percent from 1970 to 1980 (Wuebbles et al. 1983). Not all models predict the same trend, since results depend sensitively on the chemical schemes used in the tropospheric model (see WMO 1982a).

The increasing concentrations of ozone in the lower atmosphere over the Northern Hemisphere pose potential risks to air quality over the surface of the globe. The source of the additional ozone may be photochemical production within the troposphere, or may result from increased transport from a perturbed stratosphere.

Revised Chemical Models for Ozone

The most significant recent change in modeled concentrations of ozone has been caused by the new values for O_2 absorption cross sections. The change in ozone is double-edged: less dissociation of O_2 in the upper stratosphere reduces ozone concentrations around 40 km, and the increase in ultraviolet solar radiation below 25 km raises odd-oxygen production in the lower stratosphere by a substantial percentage (Froidevaux and Yung 1982, Crutzen and Schmailzl 1983, Ko and Sze 1983). This effect can be seen in Figure 5-13. The decrease in ozone above 40 km introduces another discrepancy from radiative-convective models in which ozone and temperature are coupled. Reduced ozone heating results in a calculated temperature for the stratopause that is about 10 degrees lower than the observed value (A.J. Owens, Du Pont, personal communication, 1983). It is possible that the problem with ozone above 40 km is related to the absolute calibration of the instruments and that the excess ozone below 25 km can be explained in terms of the poor parameterization of downward transport by 1-D and 2-D models in the lower stratosphere. The adoption of the new O_2 cross sections makes the agreement between current models and observations poorer.

Overall the new photochemical models--which still show that NO_x is the dominant catalytic agent for ozone destruction--seem to have resolved some of the discrepancies noted in previous reports (NRC 1982, WMO 1982a). However, they introduce a new problem in the calculated profiles of ozone. Effort must be made to test the chemical models--in at least two dimensions--against the improved climatologies now available for ozone.

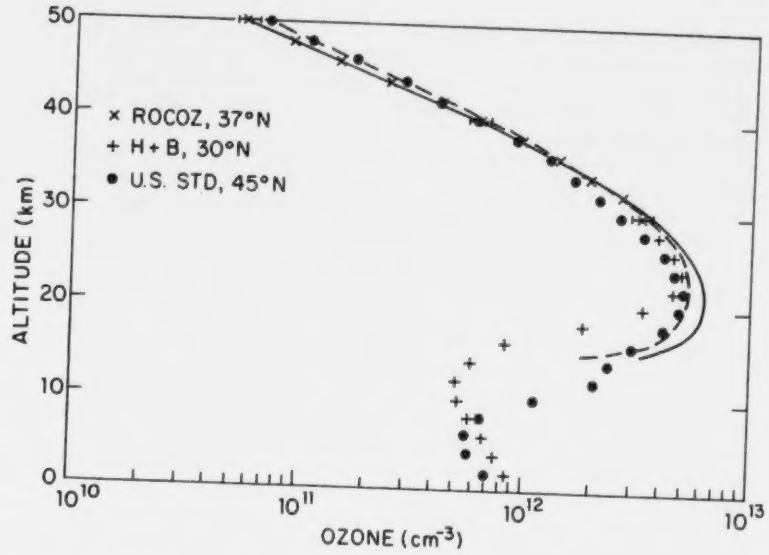

FIGURE 5-13 Effect of change in absorption cross section of O_2 on calculated (Harvard 1-D model) ozone profile. Solid curve is new profile; dashed curve is calculated with 1981 chemistry. SOURCE: See NRC (1982) for description of data and model.

RESEARCH RECOMMENDATIONS

- We should continue to develop the capabilities of multidimensional models of the atmosphere. These models are essential for the interpretation of some of the observational data in a three-dimensional context. The goal of coupling chemistry with a general circulation model is important, though as yet unattainable. A coupled, 3-D model represents the only means by which we may reliably simulate the chemistry of a significantly perturbed stratosphere in which the circulation patterns are changing due to the redistribution of ozone.
- It is important to validate and calibrate more accurately the existing 2-D models, since they should be able to simulate the seasonal and latitudinal behavior of ozone and other trace species in the current atmosphere.
- The detection and prediction of trends in ozone are a focus of this report. It is now clear that efforts at verifying perturbations to the atmosphere should be

directed toward the detection of changes in ozone in the upper stratosphere. The importance of tropospheric ozone, however, should not be ignored; we must also continue to model and observe significant changes in the lower atmosphere.

- The overall effort at comparison of theory with observation must continue. Especially promising are those studies that attempt to remove the noise in observational data that is associated with spatial variations. A more accurate calibration of local ozone concentrations of models with observations is important, especially as an aid to understanding the chemistry and dynamics of the lower stratosphere, an area of great uncertainty in the current models.
- A prime focus of the validation of photochemical models must continue to be the systematic collection of observational data that can define the local chemical systems within the stratosphere. In this framework we regard as essential the simultaneous observation of several long- and short-lived species, for example, O_3, O, OH, H_2O, HNO_3, NO, NO_2, Cl, and ClO.

6

Chemical Perturbations

INTRODUCTION

Our understanding of chemical processes in the stratosphere has improved in the past two years. When applied in theoretical models of the atmosphere, the current set of chemical kinetic and photolytic rate coefficients (Chapter 2) has led to revisions in our estimates of ozone perturbations caused by human activities. The revisions have resulted in better agreement between model calculations and observations in some cases while in other cases, the agreement remains poor (Chapter 5).

A number of atmospheric trace species that can affect ozone--including NO_x, N_2O, CFCs, CH_4, and CO_2--may be expected to vary and often are observed to be changing. Many, if not all, of these substances are simultaneously under human influence. The combined effect of these agents on ozone is complicated by chemical and physical interactions. For example, the composition, temperature, and dynamics of the atmosphere are interrelated through the absorption of sunlight (particularly by ozone in the stratosphere) and the redistribution of this energy by the circulation of air and by transfer of infrared radiation. Accordingly, atmospheric scientists have only recently begun to consider interactive physical/chemical systems and the effects on ozone of combinations of releases of several trace gases. In this report, we can only highlight the current status of the latest achievements and note that future attempts to model stratospheric ozone and its changes are likely to be more accurate than existing assessments.

In the following sections, we first review the status of model calculations for the perturbation of ozone associated with releases of individual pollutants, such

TABLE 6-1 Sensitivity of Total Column Ozone to Perturbing Influences

Trace Gas and Magnitude of Perturbation	Typical Estimate of Ozone Column Change[a] (%)	Atmospheric Lifetime (years)	Principal Mode of Pollutant Removal
CFC-11 and -12 (1980 release rates)	−2 to −4	50-150	Photolysis of CFCs in middle stratosphere
Other halocarbons (2 ppbv Cl_x increase)	~−1	1-15	Decomposition of tropospheric chlorocarbon reservoir by reaction with OH
Subsonic aircraft (2×10^9 kg NO_2/yr @ 12 km)	~+1	<1	Conversion to nitric acid and removal to surface
N_2O (20% increase by 2050)	~−4	100	Photolysis in stratosphere
CH_4 (doubling)	~+3	10	Reaction with tropospheric OH
CO_2 (doubling)	+3 to +6	?	Uptake by oceans, sediment, and biosphere

NOTE: Estimated using 1-D photochemical models.

[a] Steady-state change.

as those shown in Table 6-1. Then we turn to more realistic and more complicated cases of the calculated trends in ozone caused by simultaneous changes in several perturbing agents. We conclude the chapter with a brief discussion of uncertainties and a list of recommendations for research.

PERTURBATIONS DUE TO INDIVIDUAL AGENTS

The results of 1-D model calculations of the steady-state release of individual gases and their eventual effect on total column ozone are listed in Table 6-1. The calculations employed the most recent chemical rate parameters (Chapter 2) and assumed that only the indicated perturbing agent was acting. The effects of some combinations of time-dependent perturbations are discussed later in the chapter. The range of values given in the table encompasses the results of different research groups. The differences are due primarily to techniques of calculation and specification of boundary conditions, not to differences in the sets of photochemical reactions used. The ranges indicate only the precision of the art of modeling rather than the uncertainty associated with the results.

The estimates of ozone perturbations given in the table reflect the fact that recent calculations have yielded substantially smaller ozone reductions due to CFC releases and larger reductions from releases of N_2O (or equivalently from injection of NO_x at altitudes greater than 17 km). The effects of simultaneous increases in CFCs, N_2O, NO_x, and CH_4 may not be easily deduced from the table. The photochemical reactions controlling ozone in the stratosphere involve closely coupled, nonlinear interactions among the chlorine species, the odd-nitrogen species, methane, and water vapor. In addition, these reactions are also affected by the temperature and thus respond to increases in concentrations of the "greenhouse" gases, such as CO_2, which lower stratospheric temperatures. Injection of NO_x by subsonic aircraft at altitudes below 13 km leads to an increase in ozone concentrations in the lower atmosphere and possibly near the surface.

Halocarbons

According to the best current theoretical estimates, continuing production of CFCs at rates of 310,000 metric tons of CFC-11 and 430,000 metric tons of CFC-12 annually (roughly the 1980 production rates) considered in isolation would lead to a steady-state reduction in total column ozone of 2 to 4 percent (M.K.W. Ko, Atmospheric and Environmental Research; A.J. Owens, Du Pont; D.J. Wuebbles, Lawrence Livermore National Laboratory; and J.A. Logan, Harvard University; personal communications; 1983). We note that this set of calculations was performed for a highly restrictive set of physical and chemical parameters that represent recent, published data but are not unanimously accepted by all research groups. These calculations do not include temperature feedback effects; if they did, the calculated perturbations would increase, perhaps yielding reductions between 3 and 5 percent. A similar range in ozone reduction would be calculated if we were not to adopt the recently reported rate for the reaction of O and ClO (see Chapter 2). If we were to poll the various research groups to determine what each believes to be their "best" or "preferred" model results, we would probably find variations in opinion about the best values for the photochemical rate parameters and correspondingly a larger range in the calculated ozone reductions associated with CFCs. A much wider range would apply to the estimates if all the uncertainties in the predictions were taken into account.

Steady-state ozone reductions due to releases of CFCs are shown as a function of altitude for both "old" and "new" photochemical reaction schemes in Figures 6-1 and 6-2. In the upper stratosphere (above 30 km), the ozone reductions are very similar, and both sets of chemical reactions exhibit the well-known maximum in the relative ozone depletion profile near 40 km.

Below 30 km, however, the calculated changes in the ozone profile are dramatically different. The "new" chemistry scheme in fact yields substantial ozone increases, rather than the small increases or decreases found with older chemical reaction schemes. The major differences between the current and earlier chemical schemes are reflected in reduced concentrations of OH below 30 km with a consequent increased importance of NO_x (NRC 1982), the reduced rate coefficient for the O + ClO reaction, and the reduced absorption cross section for O_2 (Chapter 2). Using the lower cross section in recent models resulted in significantly greater radiative self-healing of the ozone column. In this effect, the reduction of ozone in the upper stratosphere allows greater penetration of sunlight in the Herzberg continuum into the lower stratosphere, thereby increasing production of ozone.

The history of model calculations of steady-state changes in the total ozone column due to CFC releases is summarized in Figure 6-3. There have been wide variations in the magnitude of the calculated ozone change and in the perception of the uncertainty in the predictions (such as 95 percent confidence interval of 5 to 26 percent given in NRC [1979]).

Reductions in total ozone caused by release of other chlorocarbons of industrial origin such as CCl_4 and CH_3CCl_3 may amount to about 1 percent at steady state (WMO 1981, Wuebbles 1983, see Table 6-1).

In many ozone perturbation estimates, releases of CFCs are assumed to remain essentially constant for 100 to 200 years so that a steady-state is eventually achieved. Clearly, this assumption may not apply in the long term. Figure 5-1 illustrates the recent history of estimated worldwide releases of CFCs. The estimated world produc-

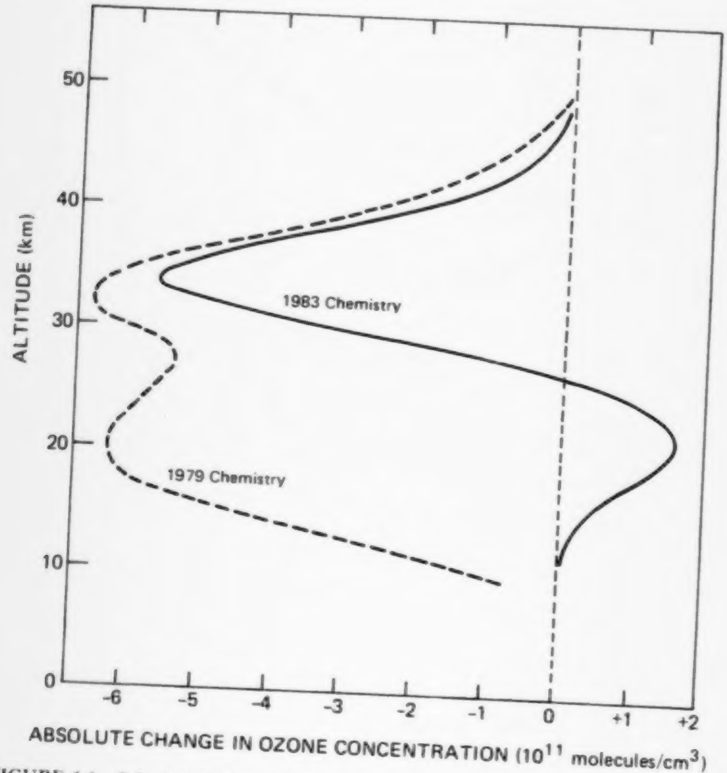

FIGURE 6-1 Calculated values of the absolute steady-state reduction in ozone concentration as a function of altitude for continuous releases of CFCs alone at 1980 rates. SOURCE: Adapted from Turco (1984).

tion of CFC-11 and CFC-12 was roughly constant between 1977 and 1982 (Chemical Manufacturers Association 1983). The estimate consists of two parts: reports of actual production from companies in North America, Western Europe, and Japan, and projections of production for Eastern Europe and the Soviet Union. In the absence of production data, the latter contribution has been assumed to rise at a rate of 18 percent per year. Western production accounted for more than 80 percent of the total worldwide production in 1982.

Wuebbles (1983) has calculated time-dependent ozone depletions for 18 halocarbon release scenarios using a

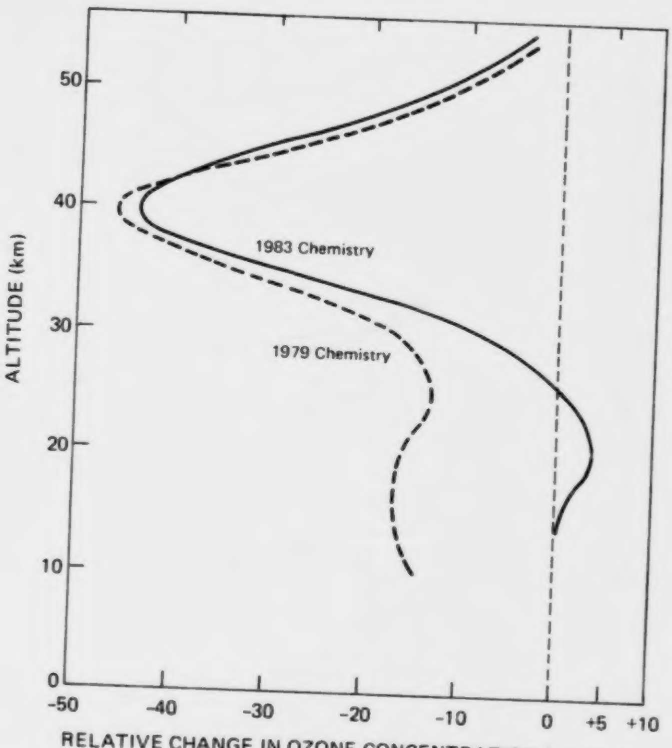

FIGURE 6-2 Calculated values of the relative change in steady-state ozone concentration as a function of altitude for continuous releases of CFCs alone at 1980 rates. SOURCE: Adapted from Turco (1984).

chemical model appropriate to the 1982 chemistry, as shown in Figure 6-4. (Thus, Wuebbles's calculations predict larger ozone depletions than do models using the most recent chemistry.) In scenarios projecting variations in CFC release rates of as much as 3 percent per year, the accrued (not steady-state) column ozone reductions by the year 2030 range from 1 to 9 percent. In each scenario the designation CLC includes CCl_4, CH_3CCl_3, and several CFCs (-11, -12, -22, -113, -114, and -115). The results emphasize that the buildup and decay of halocarbon effects occur over long time scales (Table 6-1) and that ozone depletion is very sensitive to growth in the rate of chlorine emissions.

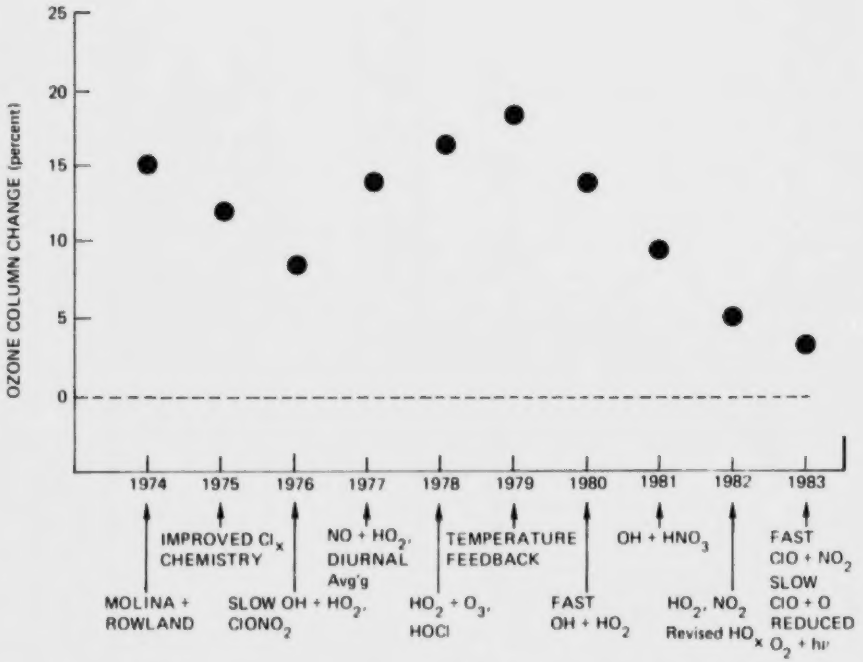

FIGURE 6-3 Estimates of steady-state reductions in total column ozone for continuous releases of CFCs at approximately 1975 rates as calculated from different chemical models. Changes in the models and simulation techniques are indicated in chronological order. SOURCE: Adapted from Turco (1984).

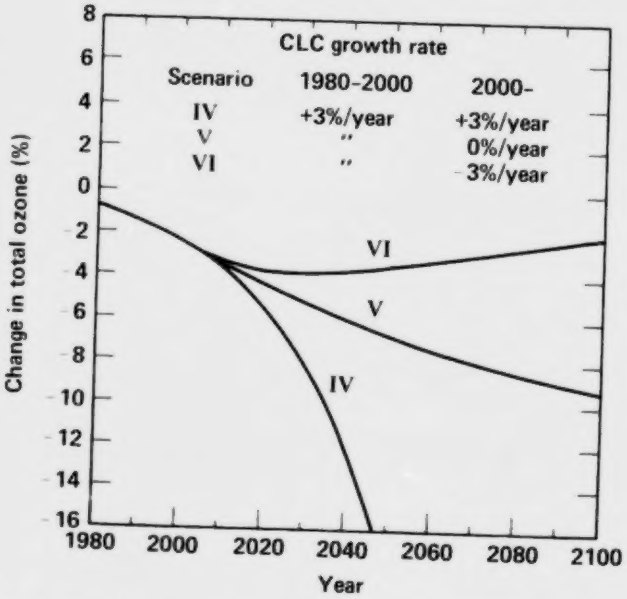

FIGURE 6-4 Time dependence of total column ozone calculated for several scenarios of CFC releases using 1982 chemistry. Calculations using more recent chemical models would yield smaller reductions in total ozone. See text of this chapter for explanation of the scenarios. SOURCE: Wuebbles (1983).

According to Cicerone et al. (1983), the response of total column ozone to chlorine injections is nonlinear, which, if true, would affect our ability to forecast changes in the total ozone column over the next decade. The extent of the nonlinearity is sensitive to the details of the model, particularly to the transport rate in the lower stratosphere (A.J. Owens, Du Pont, personal communication, 1983).

Variations in a future ozone depletion as a function of season and latitude would affect the magnitude and impact of the corresponding changes in exposure to UV-B. Unfortunately, we are only beginning to obtain reliable 2-D model predictions with the most recent photochemical model. Existing calculations suggest that larger reductions in total ozone will occur at high latitudes and that large seasonal variations in the ozone depletion are also possible at high latitudes (e.g., Steed et al. 1982, Whitten et al. 1983). The variations appear to be smaller with the 1982 chemical model than with the previous chemical models (Whitten et al. 1983). It is essential to develop and validate models that will be able to describe future changes in UV-B exposure with latitude and season.

Oxides of Nitrogen

Crutzen (1970) and Johnston (1971) discussed the connection between injections of NO_x into the stratosphere and ozone perturbations, bringing the scientific community to focus on the ozone problem. The nitrogen oxides NO and NO_2, taken together, are generally referred to as NO_x. The "odd-nitrogen" family, which is often denoted by NO_y, consists of a much larger group of species including NO, NO_2, NO_3, N_2O_5, HNO_2, HNO_3, HO_2NO_2 and $ClONO_2$. Nitrogen oxides are emitted into the lower stratosphere and upper troposphere (roughly below 13 km) by subsonic commercial aircraft. The emissions of NO_x have been thoroughly investigated and quantified (e.g., CIAP 1975, NRC 1975, Bauer 1979). At the relatively low altitudes of injection, photochemical reactions of NO_x in the presence of hydrocarbons generate small amounts of ozone in processes similar to those occurring in urban smog (WMO 1982c).

Current and projected levels of commercial aviation might increase the total column ozone burden by perhaps 1 percent (WMO 1982a, Wuebbles et al. 1983). Inasmuch as these estimates involve model calculations in the vicinity of the tropopause, where photochemistry is poorly understood and dynamics is poorly represented, such projections must be viewed with extreme caution.

More than a decade ago projections of large fleets of supersonic aircraft (SSTs) flying at 20 km raised the deep concern of atmospheric scientists (Johnston 1971). Large stratospheric ozone depletions were forecast (CIAP 1975). However, an economical supersonic air transport system has not materialized and apparently will not be developed in this century. The SST problem is not considered further in this update, but it must be remembered that large injections of NO_x at altitudes above about 17 km could result in significant reductions in stratospheric ozone.

Nitrous Oxide

Nitrous oxide (N_2O) is a long-lived atmospheric constituent that enters the stratosphere and is photochemically decomposed. One pathway for the decomposition leads to the formation of NO_x. The sources and sinks of N_2O--and the human role in the N_2O cycle--are controversial (Weiss and Craig 1976, McElroy et al. 1977, Weiss 1981, Keller et al. 1983). The stratospheric decomposition of N_2O into NO_x occurs primarily in the middle stratosphere (between 20 and 40 km). In this region, catalytic destruction of ozone by NO_x is most efficient, and increases in N_2O will result in decreases in stratospheric ozone. The effect of N_2O on stratospheric ozone can be illustrated by increasing the background N_2O concentration by 20 percent, from about 300 ppbv to 360 ppbv. Such an occurrence is expected if the currently observed rate of increase of N_2O concentration (Weiss 1981, Prinn et al. 1983a,b) were to continue over the next 100 years. Typical, recent estimates (WMO 1982c, Whitten et al. 1983, Wuebbles et al. 1983) place the resulting ozone reduction at about 4 percent of the total column (Table 6-1). Future atmospheric N_2O levels cannot be forecast with confidence, but it is apparent that potentially large ozone depletions could result if the current trend accelerates (Crutzen 1976; Liu et al. 1976; McElroy et al. 1976, 1977).

Methane

Methane concentrations in the atmosphere currently appear to be increasing at a rate of as much as 2 percent per year (Rasmussen and Khalil 1981a, Blake et al. 1982, Seiler 1982, Ehhalt et al. 1983). Methane affects stratospheric ozone by interacting in a complex manner with the chlorine and hydrogen cycles. For example, methane acts to convert ozone-reactive chlorine atoms into HCl, which does not affect O_3 directly. Hence, an increase in CH_4 leads to a decrease in free chlorine (Cl and ClO). The result is that the chlorine-induced reductions of ozone (associated with CFCs) are lessened. Methane photodecomposition products also interact with NO_x to produce ozone. In addition, HO_x and H_2O are generated from CH_4, implying further coupling of methane with all of the major chemical cycles of the stratosphere.

If CH_4 were eventually to double from current values, the total ozone column could increase by roughly 3 percent (Owens et al. 1982a, Nicoli and Visconti 1983, A.J. Owen, Du Pont, personal communication, 1983).

Carbon Dioxide

Carbon dioxide (CO_2) provides the dominant heat sink for the middle atmosphere through emission of infrared radiation to space (NRC 1983). Thus, changes in CO_2 concentrations alter the heat balance and temperature of the stratosphere and thereby the rates of basic chemical reactions. Through these reactions, which control the steady-state abundance of ozone, the ozone concentration is sensitive to temperature, generally decreasing as temperature increases. Ozone in turn provides the primary heat source for the stratosphere through the absorption of near-ultraviolet solar radiation. As a result, O_3 and CO_2 are coupled: a CO_2 increase lowers the stratospheric temperature and leads to increasing ozone concentrations, heating, and thus a partial compensation of the reduction in temperature. Increasing atmospheric CO_2 along with other trace gases such as CFCs, CH_4, and N_2O (WMO 1982b) also produces a greenhouse warming in the troposphere, which may alter the exchange of air between stratosphere and troposphere, and increase tropospheric water vapor concentrations, ultimately affecting the chemistry of global ozone perturbations (WMO 1982c, Callis et al. 1983). Estimates of the net perturbation of stratospheric ozone resulting from a doubling of atmospheric CO_2 are given in Table 6-1; an increase of several percent appears to be possible (Callis et al. 1983, Wuebbles et al. 1983).

SCENARIOS INVOLVING COUPLING OF SEVERAL TRACE GASES

Based on the preceding discussion, it is evident that when the concentrations of a number of trace gases change simultaneously in the atmosphere, the net effect on ozone may be quite complicated. The effects of individual gases differ, some causing reductions in the total ozone column (CFCs, stratospheric NO_x, N_2O) and others leading to net increases (tropospheric NO_x, CH_4, CO_2). The altitude region in which ozone is most perturbed depends on the individual species. These species are currently observed to be accumulating in the atmosphere at different rates. Several recent model studies have reported effects on ozone of the combined releases of several compounds (WMO 1982a, Callis et al. 1983, Nicoli and Visconti 1983, Sze et al. 1983, Wuebbles et al. 1983). Thus, we should consider the projections of multiple-species scenarios in assessing possible changes in stratospheric ozone in the future.

Figure 6-5 is illustrative of calculations of ozone column changes corresponding to a combination of emissions (Wuebbles 1983). The scenarios assume that (1) releases of CFCs, CH_3CCl_3, and CCl_4 (designated CLC) are constant at 1980 levels; (2) N_2O increases at 0.2 percent per year; (3) CO_2 increases at 0.6 percent per year; and (4) aircraft emissions of NO_x below about 13 km increase by a factor between 5 and 6 from 1975 to 1990 and remain constant thereafter. The calculations employed 1982 chemistry and assumed a constant flux of methane from the surface. (The examples that follow consider only NO_x released by subsonic commercial aircraft below about 13 km; that released at higher altitudes--for example, from supersonic aircraft--would have a quite different effect, acting to decrease ozone concentrations.)

According to Figure 6-5, a relatively comprehensive multiple-species emission scenario (e.g., labeled CLC + NO_x + N_2O + CO_2) leads to a fraction of 1 percent increase in the total column ozone by the year 2050. When projected increases in the methane concentration are included and the latest photochemical rate coefficients are used, the increase in total ozone is roughly 2 to 3 percent (D.J. Wuebbles, Lawrence Livermore National Laboratory, and A.J. Owens, Du Pont, personal communication, 1983).

Two important facts emerge: (1) future ozone changes associated with CFCs may be drastically altered when other perturbing effects are included, and (2) net ozone changes may be extremely difficult to detect, as counteracting effects tend to reduce the perturbation signal in total ozone. Detection of ozone changes at this level will be especially difficult over and above natural variations. However, the future scenarios for the combination of trace gases must be regarded with great caution. The sources of some of the gases may be anthropogenic as well as biogenic, and are not clearly defined or predictable.

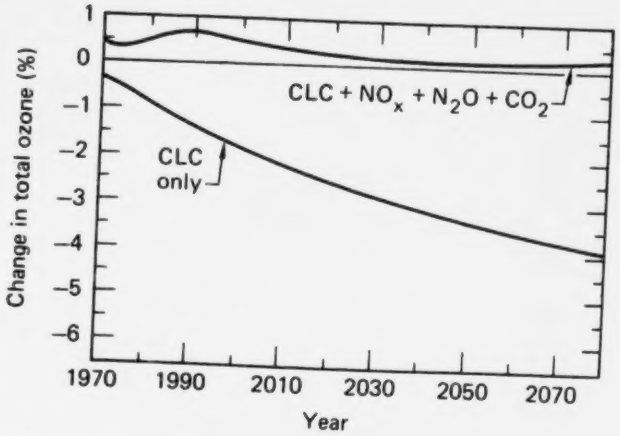

FIGURE 6-5 Time dependence of total column ozone calculated for several scenarios of combinations of species variations with constant methane and temperature coupling using 1982 chemistry. Calculations using more recent chemical models would yield smaller reductions in total ozone. See text of this chapter for an explanation of the scenarios. SOURCE: Adapted from Wuebbles (1983).

The change in the vertical distribution of ozone for the CLC + NO_x + N_2O + CO_2 scenario of Figure 6-5 is shown in Figure 6-6. It is apparent that the large ozone depletion above about 25 km (due mainly to CFCs) is offset by an equivalent ozone increase at lower altitudes. A cautionary note is in order, however. Wuebbles et al. (1983) argue that the large uncertainty in the predicted CO_2 effect may cause an overestimate of the ozone increase with CO_2 emission. Callis et al. (1983) present similar results for steady-state simulations of CFC injections both with and without a doubling of CO_2. Their model attempts to simulate the response of tropospheric composition to temperature changes (notably, through changes in water vapor concentrations).

Figure 6-7 further illustrates the sensitivity of calculated values for the future change in the ozone column to assumptions about the scenarios. The figure shows recent results of groups at Atmospheric and Environmental Research (AER) and Du Pont (N.D. Sze, AER, and A.J. Owens, Du Pont; personal communications, 1983), using scenarios for CLCs, CO_2, N_2O, and NO_x similar to those of Wuebbles (Figure 6-5), but with the more recent chemistry. While Wuebbles assumed a constant flux of

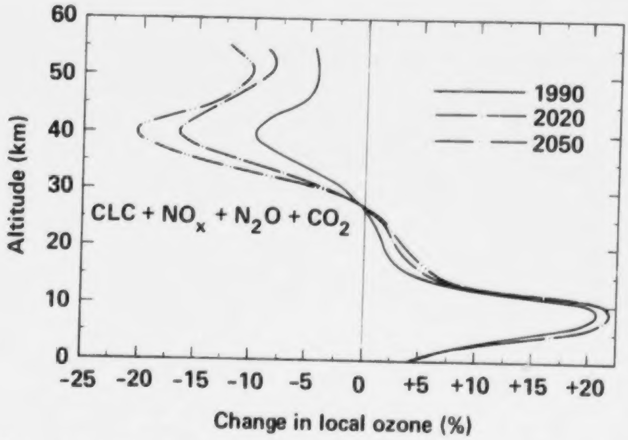

FIGURE 6-6 Time dependence of the vertical distribution of ozone concentration for one of the combination scenarios of Figure 6-5. See text of this chapter for an explanation of the scenario. SOURCE: Adapted from Wuebbles (1983).

methane at ground level, AER and Du Pont assumed that the flux increases at 1.2 and 1.5 percent per year, respectively. The sensitivity of the calculations to assumptions about the release rate of methane is clearly illustrated in the figure.

Caution should be exercised in assessing the appropriateness of scenarios for changes in the concentrations of trace gases. For example, the increases in N_2O, CH_4, and CO_2 may vary independently. It is conceivable that improved technology or changing economic conditions might lead to renewed interest in commercial supersonic transport. Similarly the assumption of constant production and release of CFCs and other halocarbons may be unrealistic in view of their increasing industrial use in a growing world economy.

Seasonal and latitudinal changes in ozone for multiple-species perturbations are not available from the most recent chemical models. Latitudinal and seasonal modulations in total column ozone will affect the biological impact of the associated UV-B changes.

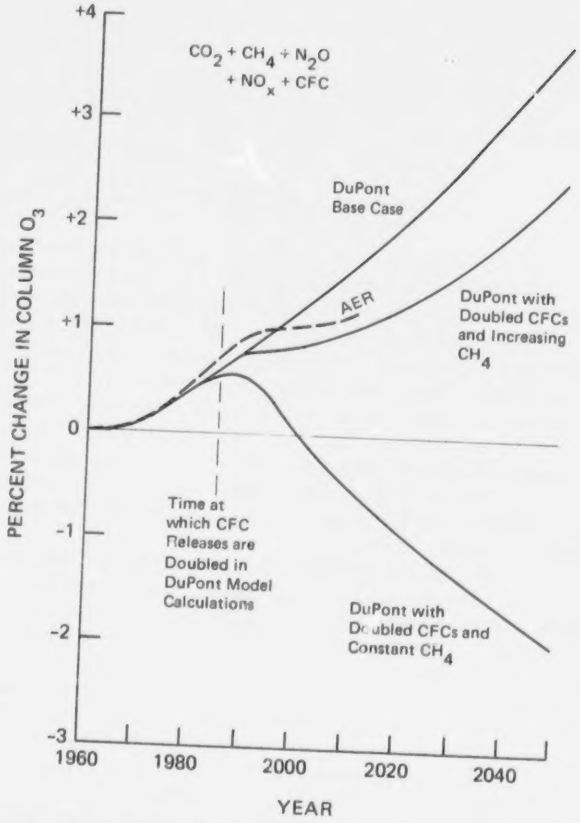

FIGURE 6-7 Time dependence of total column ozone in multiple-perturbation scenarios using 1983 chemistry. SOURCE: A. J. Owens, Du Pont, personal communication, 1983.

The Greenhouse Effect

Chemical compounds that affect stratospheric ozone may also produce a greenhouse effect that can alter tropospheric temperatures and consequently the other chemical and physical properties of the troposphere (WMO 1982c, Callis et al. 1983, NRC 1983). While such tropospheric alterations are important in their own right, through coupling processes, they may lead to additional modifications in the ozone column. The relative importance of various tropospheric gases to the greenhouse effect can be estimated using radiative-convective and general circulation models. However, accurate calculations of the tropospheric response to the radiative changes, including the effects on temperature and wind patterns, are not yet available.

UNCERTAINTIES

Uncertainties in assessments of ozone perturbations are difficult to discuss quantitatively. In their treatment of uncertainties, earlier assessments have varied widely--from the detailed (NRC 1975, 1979; NASA 1977, 1979a) to the casual (NRC 1976a,b, 1982; WMO 1982a). The detailed treatments often leave the wrong impression that the actual sources of uncertainty are well defined. For example, it is not clear how one determines the "uncertainty" associated with the use of 1-D models, as compared with that for 2-D or 3-D models (NRC 1979). In accordance with these limitations, only a qualitative statement of uncertainty is made here.

In the current predictions of ozone change, the major areas of uncertainty are (a) release-rate scenarios, (b) photochemical processes and rate coefficients, (c) radiative-dynamical effects and interactions. Forecasts of future concentrations of trace gases can be made with a reasonable degree of confidence from the historical record only over relatively short time spans. Nevertheless, we must make the best estimates of future conditions and the atmospheric consequences, recognizing that uncertainty grows as we project into the future.

The uncertainties in chemical rate constants can be analyzed quantitatively and have been reduced from those cited in NRC (1979). No analyses of the sensitivities of model results to changes in the rate coefficients have been performed recently. The uncertainties due to possible systematic errors associated with major oversights in current photochemical schemes continue to exist, but the likelihood of major omissions decreases as research continues.

Additional uncertainty, not easily quantified, is associated with deficiencies in the models used to predict ozone change. For example, most predictions are based on 1-D or 2-D models, which attempt to simulate the average effects of transport, but do not correctly represent the detailed mechanisms of atmospheric dispersion and removal of pollutants. Moreover, these models are unable to take into account all the radiative-dynamical feedback and coupling mechanisms that apply when the atmosphere is perturbed. Perhaps fortuitously, currently calculated ozone changes in the lower stratosphere (below 30 km) tend to cancel CFC-induced reductions in the upper stratosphere, but this partial cancellation does not reduce the uncertainties of the models and theory.

IMPLICATIONS FOR UV-B INSOLATION

The intensity of solar ultraviolet light at the Earth's surface may be estimated using a radiative transport model that takes into account absorption by O_3 (and other gases), molecular Rayleigh scattering by N_2 and O_2, aerosol scattering and absorption, and cloud opacity (CIAP 1975). The results are sensitive to a number of parameters, including the solar zenith angle, and hence latitude and season. To determine the "effective" biological UV-B dose, the UV-B flux at the ground must be weighted by an "action spectrum" for a particular organism and biophysical effect, and integrated over wavelength and over the appropriate time interval,

$$D = \int \dot{D}\, dt = \int \left\{ I(\lambda, t, z = 0) S(\lambda) d\lambda \right\} dt$$

where D is the dose in appropriate units, D is the dose rate, I is the total flux of sunlight at the ground, and S is the action spectrum as a function of wavelength λ. Typically, it is found that the average fractional increase in UV-B dose rate is approximately one to three times the fractional decrease in the total ozone column (CIAP 1975, Gerstl et al. 1981, Steed et al. 1982). That is, a 1 percent decrease in ozone causes a 1 percent to 3 percent increase in UV-B dose rate. For example, the dosage factor for the Setlow DNA absorption spectrum is about 2.6 averaged over latitude and season according to Gerstl et al. (1981). The biological implications of increased UV-B irradiation are discussed in Part II, which also contains more detailed discussion of the action spectra.

RESEARCH RECOMMENDATIONS

- Emissions, inventories, and lifetimes should be defined for the key species that affect ozone, directly or indirectly, such as halocarbons, N_2O, NO_x, CH_4, and CO_2.
- Models that couple radiation, dynamics, and photochemistry in comparable detail should continue to be developed. Both the dynamical and the chemical mechanisms that couple the trace gases of the stratosphere and troposphere need to be examined.
- The observational evidence for changes in stratospheric ozone over the past decade need to be evaluated and attempts to define similar trends in important background gases, such as N_2O, NO_x, CH_4, and other hydrocarbons, CO, and stratospheric H_2O should be continued.
- Techniques need to be developed for the quantitative analysis of uncertainties in theoretical models, particularly their sensitivity with regard to the chemical kinetic scheme and the parameterization of dynamical transport.

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PART II
Effects on the Biota

7

Introduction and Summary

This part of the report examines the effects of an increase in the amount of solar radiation of wavelengths in the ultraviolet-B (UV-B) band that would reach the Earth's surface as the result of a reduction in the total amount of ozone in the atmosphere. While in Part I we concluded that the long-term change calculated for the total amount of ozone above the Earth's surface could be either negative or positive, research on biological effects of changes in exposures to UV-B has focused exclusively on effects of increases in the flux of UV-B due to reductions in total ozone. Consequently, in this part of the report we examine only the potential effects of increasing the UV-B flux. This focus is the result of the fact that only recently has the possibility been raised that perturbations of the stratosphere might lead to net increases in total ozone.

The effects considered include those on humans, other animals, marine life, and plants. Changes in the spatial distribution of ozone in the stratosphere could also lead to changes in the Earth's climate, but the nature and effects of these changes are currently unknown and are not considered here.

A broad spectrum of electromagnetic radiation (light) from the sun impinges on the Earth's upper atmosphere. The fraction of this radiation that reaches the biosphere on the Earth's surface depends on its wavelength (or energy), the season, cloud cover, and other factors, such as the amount of ozone, one of the more important UV-absorbing substances in the atmosphere. Humans sense, or are affected by, electromagnetic energy in different regions of the spectrum in distinctly different ways. For this reason and others, it is convenient to describe

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TABLE 7-1 Spectrum of Solar Radiation Reaching the Earth's Surface

Electromagnetic Energy	Range of Wavelengths (nm)	Approximate Percentage of Total Solar Radiation Reaching Surface
Infrared	800-20,000	50-60
Visible light	400-800	30-40
Ultraviolet	200-400	2-3

the sunlight spectrum as comprising three regions: ultraviolet, visible, and infrared (Table 7-1).

Ozone molecules absorb radiation in the ultraviolet (UV) band, which commonly is divided into three regions: UV-A, wavelengths in the range of 320 to 400 nm; UV-B, the 280 to 320-nm range; and UV-C, the 200- to 280-nm range. In general terms, ozone absorbs radiation strongly in the UV-C band and little, if at all, in the UV-A range. In the UV-B band, absorption by ozone is a sensitive function of wavelength, increasing as wavelength decreases.

Life on Earth is directly and indirectly dependent on solar radiation as its source of energy. All living organisms require energy in a usable chemical form for metabolic activities associated with growth, development, and reproduction. The process of photosynthesis in green plants converts solar energy, carbon dioxide, and water into carbohydrates rich in energy. Organisms that cannot produce their own energy through photosynthesis must participate in a food chain that includes plants that can.

Wavelengths of light in the 400- to 800-nm range are absorbed by the rods and cones of the human retina and are perceived as visible light. Radiation of longer wavelengths is sensed as heat. Wavelengths in the UV-B range are absorbed by the human skin and are used in part to drive the synthesis of vitamin D, which is necessary for normal bone metabolism. Negligible ultraviolet energy in the range of 200 nm to 280 nm reaches the Earth's surface.

Not all the effects of solar radiation, however, are beneficial to humans, other animals, or plants. Light in the UV-B band has been found to be absorbed by cells and to be associated with diverse and often deleterious biological effects. In humans these effects range from mild sunburn to skin cancer (see Chapters 8 through 10). In other organisms, such as certain plants and marine life, exposure to UV-B radiation may adversely affect development and reproductive success (see Chapters 13 and 14). In animals, numerous skin diseases are caused or aggravated by exposure to the sun.

A working classification of diseases of the skin of humans induced or aggravated by ultraviolet light is shown in Table 7-2. The table indicates those diseases known to be associated in some way with UV-B radiation and those associated with either visible light or UV-A radiation; the region of the spectrum affecting the other listed diseases is not known.

In this part of the report we are concerned not with the causes of changes in UV-B energy reaching the Earth, but with estimating the biological response to changes should they occur. Exposure to UV-B radiation may also change for reasons unrelated to changes in stratospheric ozone. For example, changes in human life-styles or fashions can result in more exposure of the skin to UV-B, and shifts in populations to areas with sunnier climates may have consequences for the overall exposure of the population to UV-B.

Whatever the causes of increased exposure, its biological consequences begin with absorption of UV-B by specific molecules, such as DNA or cellular proteins. Absorption of UV energy increases the internal energy of the molecule. The added energy is sometimes harmlessly emitted as heat, fluorescence, or phosphorescence, but in other cases chemical changes can occur that permanently alter the nucleus, cytoplasm, or membrane of the living cell.

NRC (1982) identified four underlying biological questions that bear directly on our ability to predict responses of living systems to changes in their exposure to ultraviolet radiation:

1. What is the relationship between the dose of electromagnetic radiation in a specific region of the spectrum and the resulting biological effect? The relationship defines the dose-response curve.
2. For a given response, is there a reciprocal relationship between the intensity of the radiation and the duration of exposure that together define the dose?
3. How does biological sensitivity depend on wavelength, i.e., what is the weighting function, or action spectrum, that describes a given biological effect?
4. Are there interacting effects at different wavelengths?

TABLE 7-2 Classification of Diseases of Human Skin Involving Sunlight

Type	Disease
Genetic and metabolic	Xeroderma pigmentosum[a]
	Erythropoietic protoporphyria[b]
	Erythropoietic prophyria[b]
	Erythropoietic coproporphyria[b]
	Porphyria cutanea tarda[b]
	Albinism[a]
Phototoxic and photoimmunologic	Phototoxic
	Internal (drugs)[a]
	External (drugs, plants, fruit)[a,b]
	Photoallergic
	Solar urticaria[a] (immediate hypersensitivity)
	"Drug" photoallergy[b] (delayed hypersensitivity)
Degenerative and neoplastic	Squamous cell carcinoma[a]
	Malignant melanoma
	Actinic keratosis[a]
	Basal cell carcinoma
Idiopathic	Polymorphous light eruption[a]
	Hydroa aestivale[a]
	Hydroa vacciniforme[b]
	Actinic reticuloid[a]
	Actinic prurigo
Photoaggravated	Discoid lupus erythematosus
	Systemic lupus erythematosus
	Dermatomyositis
	Herpes simplex
	Darier's disease
	Bloom's disease
	Acne vulgaris
	Atopic dermatitis
	Disseminated superficial actinic porokeratosis (DSAP)
	Lichen planus actinicus
	Pemphigus foliaceus
	Transient acantholytic dermatosis (TAD)
	Metabolic (protein and/or vitamin)
	Pellagra
	Kwashiorkor
	Hartnup disease

[a] Associated in some way with UV-B radiation either by inference from animal studies or from direct evidence in humans.

[b] Associated with UV-A or visible light.

SOURCE: Adapted from Harber and Bickers (1981).

The NRC (1982) report provided a comprehensive review of the state of knowledge of the causes and effects of stratospheric ozone reduction as of the fall of 1981. As already indicated this report updates rather than replaces the material presented in that report. Because of data recently obtained and because of the major importance of the two rapidly advancing clinical fields of malignant melanoma and photoimmunology, these topics are given major emphasis here. Some biological effects (e.g., diseases of the eye and tumors of the skin in domestic animals) are not treated in this report because little new knowledge about them has been gained in the past few years.

The major findings of Part II are summarized below, while details are provided in the respective chapters that follow. As in Part I, each chapter also contains our recommendations for further research.

SUMMARY

Immunological Changes Caused by Ultraviolet Radiation

Studies with laboratory animals have demonstrated that several immunological changes take place following exposure to UV-B radiation (see Chapter 8). For the most part, these changes decrease the effectiveness of the animal's immune response system. The suppression of the immune response is systemic. Exposure of the skin to UV-B radiation not only inhibits local allergic reactions in the irradiated skin, it also reduces or prevents certain immune reactions at distant, unexposed sites. Recent studies have demonstrated unequivocally that systemic immunological changes produced as a result of UV-B irradiation are an important factor in the development of primary skin cancers induced in mice by UV radiation.

It has now been demonstrated that at least some of these immunological changes also occur in humans exposed to natural or artificial UV radiation. Thus, the concerns expressed in the NRC (1982) report that the immunosuppression observed in UV-irradiated animals might also occur in humans were well-founded. The extent of the immunological perturbations caused by exposure of humans to sunlight--and particularly to UV-B radiation--are not yet known, and their implications for human health are not clear. A primary concern is the possibility that these immunological changes may contribute to the development and pathogenesis of human skin cancer, including malignant melanoma.

Nonmelanoma Skin Cancers in Humans

Epidemiological studies continue to support the concept that increases in UV-B dose will increase the incidence of squamous cell carcinoma and basal cell carcinoma (Chapter 9). Additional factors, not previously considered in models, may also affect predictions of future changes in the incidence of nonmelanoma cancers of the skin. Such factors include the trend toward increased longevity of the population, shifts in population to areas of higher UV-B insolation, and increases in leisure activities that involve exposure to UV-B. If continued, each of these trends suggests an increasing incidence of basal cell and squamous cell carcinomas independent of any changes in exposure to UV-B because of changes in stratospheric ozone.

Therefore, models used to predict future incidence of basal cell and squamous cell carcinomas should take these trends into consideration, along with changes in UV-B attributable to changes in stratospheric ozone. Taken together, all these factors may result in a greater increase in the incidence of nonmelanoma skin cancer in the population in the future than current models predict.

Malignant Melanoma in Humans

Malignant melanoma in humans has become a major public health problem (see Chapter 10). The incidence and mortality rates of malignant melanoma have risen consistently in the United States during the past five decades. The rate of increase in mortality is now higher than that for any malignancy except cancer of the lung. New data support the hypothesis that the risk of the development of some types of malignant melanoma is related to exposure to sunlight. Evidence that UV radiation (or UV-B) is related to malignant melanoma is only circumstantial. That other factors are also important is illustrated by the identification of a subset of the population manifesting "dysplastic" nevi that faces increased risk of development of malignant melanoma. The studies strongly suggest that genetic factors, some of which may be expressed by susceptibility to damage from sunlight, must be considered in certain types of malignant melanoma in humans. Thus, current data do not permit us to conclude that exposure to the sun is the only risk factor for all malignant melanomas.

Animal Studies of Photocarcinogenesis

Animal studies make it possible to test specified variables while holding other factors constant (see Chapter 11). Although animal skin differs from human skin in a variety of ways, the success of using animal data to predict many other photobiological responses in human skin supports their value as predictors of carcinogenic responses as well.

Recent findings from experimental studies of photocarcinogenesis in animals have improved our understanding of the four questions posed above. Evidence is accumulating that dose-response data in laboratory animals are relevant to effects in humans, and, in addition, two recently reported mathematical models have been used to predict effects of increased UV-B. The predictions of these models are similar over the range of doses for which data exist, but differ markedly at higher and lower doses. Methods to resolve these differences are currently available. Not enough information is currently available, however, to determine an equation that will accurately predict the response to more than a few of the possible conditions of UV-radiation exposure.

In the absence of a measured action spectrum for a given biological effect, several spectra for acute processes have been used as approximations. All of these spectra are qualitatively similar, but the fact that they span the shortest and most variable part of the UV-B spectrum magnifies the importance of even minor differences. Methods are available, however, for reducing uncertainties. Finally, while most data on photocarcinogenesis suggest that effects at different wavelengths are independent and additive, a few studies suggest interactive effects. The significance of the interactions is not known, but their possible relevance cannot be ignored. Methods are available to settle this issue also.

Molecular and Cellular Studies

Research at the molecular and cellular levels has provided continuous impetus and direction to studies of effects of UV-B radiation on biological organisms, including humans (see Chapte 12). Such studies have, for example, revealed that UV radiation produces a complex spectrum of damage in DNA molecules and that cells possess intricate mechanisms for repairing this damage.

Recent substantial advances in molecular biology and DNA chemistry can be applied to the elucidation of UV-B-induced damage and its repair. These advances can detect DNA alterations at specific sites within specific genes and can construct convenient assays for monitoring critical steps in the response of cells to UV radiation.

The recent discovery of the natural occurrence of left-handed DNA, or Z-DNA, in cells suggests new ways to understand how genes are controlled and why control breaks down in tumor cells. Photochemical alterations induced by UV irradiation of Z-DNA are likely not only to be different from those found in the more abundant B-DNA (normal right-handed DNA structure), but also to be possessed of special consequences. Furthermore, the absorption spectrum of Z-DNA predicts a greater propensity for damage induced by UV-B than does that of B-DNA.

Effects of UV-B Radiation on Plants and Vegetation As Ecosystem Components

Considerable experimentation in controlled-growth chambers shows that most plants, including crop plants, are adversely affected by UV-B radiation. Such irradiance stunts growth, cuts down total leaf area, reduces production of dry matter, and inhibits photosynthesis in several ways. Plants differ in their sensitivity to UV-B radiation; the most sensitive observed to date are the cucumber and its relatives in the squash family. All soybeans are sensitive, but the range of sensitivity among its varieties is wide. Resistance or sensitivity to UV-B is genetically based. Some species show ability to acclimate to increased UV dosages; others do not. Evolution of UV-resistant populations has occurred within certain species of wild plants. The mechanisms affecting sensitivity and resistance of species, as well as competitive interactions in ecosystems under UV-B stress, need continuing study. Since most research so far has been under laboratory conditions, it is imperative that field experiments be done under UV-B stress.

There is a strong natural gradient in UV-B from the polar regions to the equator. Within the arctic-alpine zone itself, the maximum integrated effective UV-B irradiance increases by a factor of more than 7 from northern Alaska to the equatorial Andes. Maximum daily total visible radiation along this same gradient, on the other hand, increases only by a factor of 1.6. Plants along this gradient have evolved protective adaptations against UV-B mainly by producing screening compounds such as flavonoids in the epidermis.

Effects of UV-B Radiation on Marine Organisms

Recent measurements of the amount of ultraviolet light penetrating ocean waters show that the major factors in the absorption of these wavelengths are both biogenic and nonbiogenic substances, whose concentrations are generally larger in coastal waters than in the open ocean. (See Chapter 14.)

Experiments have demonstrated that small changes in UV-B affect marine photosynthetic organisms, herbivores, and carnivores, suggesting that such changes could affect the entire marine food web. Experiments show that growth and associated metabolic processes are reduced and that reproduction, survival, and behavior are adversely affected with increased UV-B. Species differ markedly in their sensitivity to UV-B, but the reasons for the differences remain unclear.

8

Immunological Changes Caused by Ultraviolet Radiation

INTRODUCTION

In recent years it has become increasingly apparent that exposure to sunlight is likely to produce immunological changes in humans. The idea that exposure to sunlight could trigger certain allergic reactions (reviewed in Parrish et al. 1983) had its origin in observations made in humans in the 1940s. Many years later, studies on laboratory animals exposed to artificial sources of UV radiation demonstrated that certain immunological changes can be produced by UV-B radiation. More recently studies with human subjects have confirmed the prediction from studies in animals that the human immune system is accessible to modification by natural and artificial sunlight. Because the immune system plays such a pivotal role in maintaining the integrity of the body, protecting it from infectious microorganisms, toxic chemicals, and even certain cancers, the finding that immune responses can be perturbed by environmental radiation constitutes a serious concern.

Although a brief summary of the pertinent studies on experimental animals was included in NRC (1982), it is only very recently that the relevance of these studies to human health has been firmly established. For this reason, a review of this topic is presented here also, along with summaries of the most recent findings in humans and animals. The amount of information that has been generated just in the past two years is considerable, reflecting the intense interest in the newly emerging field of photoimmunology, which is the study of the interactions between light and the immune systems (for reviews see Kripke 1981, Parrish 1983, Parrish et al. 1983).

STUDIES ON EXPERIMENTAL ANIMALS

Because UV radiation is almost completely absorbed in the skin of animals and little penetrates beyond, its ability to modify the immune system was surprising. The finding that UV radiation can suppress some immune response originated from studies on the antigenic properties of skin cancers induced in mice by UV radiation. These cancers were found to be unusually antigenic in that they can stimulate a vigorous immune response. Upon transplantation to genetically identical mice, the majority of these tumors were so antigenic that they were rejected immunologically. This response raised the question of how such antigenic cancers were able to survive immunological destruction in the host of origin (Kripke 1974). Studies addressing this question produced the unexpected finding that repeated exposure of mice to UV radiation produced a systemic alteration that interfered with the rejection of these antigenic skin cancers (Kripke and Fisher 1976). The alteration was systemic in that exposure of dorsal skin to UV radiation rendered the mice susceptible to tumors implanted at distant, nonexposed sites. Subsequent research demonstrated that the failure of tumor rejection was due to the induction in UV-irradiated mice of suppressor cells that prevented the rejection of UV-radiation-induced skin cancers (Fisher and Kripke 1977, Spellman and Daynes 1977). These suppressor cells are T lymphocytes that serve as part of a regulatory network of cells that control the magnitude and duration of immune responses.

These findings prompted additional investigations of the immunological competence of mice exposed to UV radiation and led to the discovery of other immunological aberrations in UV-irradiated animals (Kripke et al. 1977, Jessup et al. 1978, Greene et al. 1979). The alteration that has been studied in most detail is the systemic suppression of a particular type of allergic reaction called contact hypersensitivity (CHS), which is most familiar in humans in the form of poison ivy. In this immune reaction a reactive chemical is placed on the skin, and an immune response involving T lymphocytes develops against the chemical, which is complexed with host cells and proteins. A second application of the sensitizing chemical at any site results in a severe inflammatory reaction at the site of application. This reaction is suppressed in UV-irradiated mice. The suppression is systemic in that neither the immunizing nor the eliciting dose of chemical is applied to skin that is exposed directly to UV radiation. In addition, the suppression is associated with the appearance of suppressor T cells that inhibit specifically the CHS response to the chemical applied (Noonan et al. 1981a).

A totally unrelated line of investigation revealed that certain cells residing in the skin are actually components of the immune system. Langerhans cells, which form a network throughout the epidermis, are derived from the bone marrow and are close relatives of the macrophage (Stingl et al. 1978). It was found that these cells are highly susceptible to damage by UV radiation, and that such damage can lead to depressed CHS reactions toward chemicals that are applied directly onto irradiated skin (Toews et al. 1980).

Thus, at least three types of interactions between UV radiation and the immune system have been identified to date: (1) the direct interaction between UV radiation and elements of the immune system that reside in the skin (i.e., Langerhans cells); (2) the direct interaction between UV radiation and skin that leads to the induction of new or altered antigens (i.e., tumor antigens) that can be recognized by the immune system; and (3) the indirect interaction between UV radiation and the immune system that leads to systemic suppression of certain immune responses (i.e., tumor rejection, CHS).

Direct Effects of UV Radiation on Cutaneous Components of the Immune System

Update of Research Results

In 1980 Toews, Bergstresser, and Streilein made the seminal observation that exposure of mouse skin to very small doses of UV radiation caused morphological and enzymatic changes in cutaneous Langerhans cells. Application of a contact sensitizing chemical, in this case dinitrofluorobenzene (DNFB), at the site of such altered skin induced not the expected CHS reaction but specific immunological unresponsiveness. This specific unresponsiveness is demonstrated by the failure of animals to respond to a subsequent, immunizing dose of DNFB that is applied to unexposed skin, although they can respond normally to a different chemical, e.g., trinitrochlorobenzene (TNCB), placed on unirradiated skin. This discovery directed attention toward the potential of UV radiation to interact directly with components of skin in a manner that produced systematic perturbations of the immune system. It also raised the question of whether these immunological effects of UV irradiation might play an important role in the pathogenesis of cancers that develop locally in skin exposed to UV radiation or cancers that metastasize to cutaneous sites.

Because of these important implications, considerable effort has been directed toward unraveling the mechanisms underlying the ability of UV radiation to produce immunological unresponsiveness. Recent progress has occurred on several aspects of this problem. Elmets et al. (1982) have demonstrated that the suppression of CHS is associated with the production of antigen-specific suppressor T lymphocytes. Similarly Semma and Sagami (1981) showed that application of DNFB to mouse tail skin, which is deficient in Langerhans cells, also induces antigen-specific suppressor T cells. The observations suggest that when antigen bypasses Langerhans cells, the suppressor cell pathway is activated instead of the effector cell pathway. Normally Langerhans cells take up the antigen, process it in some way, and present it in an immunologically active form to lymphoctyes, thereby initiating the CHS (effector) response (Bergstresser and Streilein 1983). After being damaged by UV radiation, Langerhans cells can no longer function in this way, and, as a consequence, the introduction of antigen triggers an alternate immunological pathway that results in suppression.

Support for this hypothesis has been provided by studies in which suspensions of epidermal cells containing Langerhans cells are exposed to UV radiation in vitro. Sauder et al. (1981) demonstrated that immunization of mice with epidermal cells that were coupled with antigen and exposed to UV radiation in vitro induced antigen-specific suppressor T cells, whereas epidermal cells that were unirradiated induced CHS. Similarly, work by other groups with antigen-presenting cells from the spleen and peritoneal cavity, as well as from skin, exposed in vitro to sublethal doses of UV radiation, were unable to trigger immune reactions in vitro (Fox et al. 1981, Stingl et al. 1981, Aberer et al. 1982). Recent studies suggest that this deficiency may be due to the failure of UV-irradiated cells to make interleukin-1 (IL-1), a chemical mediator that is required for the activation of lymphocytes (Sauder et al. 1983a, Stingl et al. 1983).

A new finding that may be relevant for studies in humans is that the ability of UV radiation to modify the immune response in this way is under genetic control. Bergstresser et al. (1983) have found that in some strains of mice, UV radiation causes morphological alterations in Langerhans cells, but application of the contact sensitizing agent produces a normal CHS reaction. Crossing a UV-sensitive mouse strain with a UV-insensitive strain produces offspring that have an intermediate level of sensitivity to UV-induced immunosuppression. One interpretation of this result is that mice of the insensitive strains have an alternative pathway for antigen presentation that bypasses the requirement for Langerhans cells (Streilein and Bergstresser 1983). Thus, inactivation of Langerhans cells by UV radiation would not interfere with antigen presentation by the alternate pathway, and hence would not lead to the induction of suppressor cells. Regardless of the underlying causes, this finding demonstrates that sensitivity to this particular effect of UV radiation is under strict genetic control. If this is a general finding for other species, it implies that certain human populations may have a genetically determined susceptibility to this immmunosuppressive effect of UV radiation, and hence may be at greater risk from the deleterious effects of UV radiation.

In the course of studies on the role of Langerhans cells in cutaneous immune responses, Katz and his associates (Sauder et al. 1982) discovered that keratinocytes, which are the most prevalent cells in the epidermis, produce a substance that helps to activate T lymphocytes. This substance, termed ETAF--for epidermal-cell-derived T lymphocyte activating factor--is now thought to be identical to the IL-1 produced by antigen-presenting cells (Sauder et al. 1983b). The finding that exposure of skin in vivo to UV radiation can inhibit the production of this substance (Sauder et al. 1983a) raises the intriguing possibility that UV radiation also may affect local immunological reactions indirectly through this effect on keratinocytes. This possibility is unproven, however, because there is as yet no direct evidence for the participation of ETAF in immune reactions in skin.

Another manifestation of the effects of UV radiation on immune reactions mediated by T lymphocytes is the observation that it is sometimes difficult to elicit cutaneous immune (allergic) reactions in UV-irradiated skin. This phenomenon differs from the suppression described above in which the sensitizing dose of antigen is applied to irradiated skin and the eliciting dose is applied at an unexposed site. In the second phenomenon animals are first sensitized, then exposed to UV radiation, and the eliciting dose of antigen is applied at an irradiated site. The effect, in guinea pigs, was first described in an isolated observation by Hanizko and Suskind (1963) and recently Morison et al. (1981) and Austad and Mork (1982) have reopened the investigation of this topic. The mechanism by which UV radiation decreases the inflammatory reaction is not known, but alterations of Langerhans cells and/or inhibition of ETAF production by keratinocytes are likely possibilities. Another, perhaps related, observation made in a rat model is that the cutaneous manifestations of graft-versus-host disease can be eliminated by treating the skin directly with UV radiation (Glazier et al. 1983). Again, these authors suggest that Langerhans cells may be the target for this effect of UV radiation, based on histological evidence. Currently, no information is available concerning the consequences of these local, UV-radiation-induced alterations for skin infections or wound healing, which are obviously important considerations in assessing the effects of UV radiation on human health.

Wavelength and Dose Considerations

The wavelengths of UV radiation that have been used to alter Langerhans cells and to prevent the induction of CHS to sensitizing agents applied to irradiated skin are mainly in the UV-B range (280 to 320 nm). The sources of UV radiation used most frequently in these studies are fluorescent sunlamps, which emit approximately 80 percent of their energy in the UV-B region of the spectrum. Preliminary studies by Elmets et al. (1983) suggest that the most effective wavelengths for inducing this form of immunosuppression are between 290 and 300 nm and that the action spectrum for this effect may be similar to that for producing erythema. This result concurs with a preliminary report by Noonan et al. (1982) on the wavelengths of UV radiation that can produce morphological alterations in Langerhans cells.

The doses of UV-B radiation required to produce this form of immunosuppression are quite minimal compared with those required to produce skin cancer; only between 200 and 800 joules per square meter (J/m^2) are needed. In terms of human responses to UV radiation, this dose of radiation represents between 1 and 4 minimal erythemal doses (MED), where 1 MED equals the amount of energy required to produce distinct reddening of Caucasian skin at a body site normally protected by clothing. Thus, in terms of both dose and wavelength, the effects of UV radiation on immune responses are highly relevant to the exposure of humans to natural sunlight. Exposure of mice to even lower doses of UV radiation can interfere with the ability of their keratinocytes to produce ETAF (Sauder et al. 1983a). An important question that remains to be addressed is the long-term consequences of multiple exposures to UV radiation. No information is available on whether the effects of multiple doses of UV radiation are cumulative over time, whether repair processes can reverse some or all of these effects, or what happens to Langerhans cells and immunological function over long periods of repeated exposure to UV radiation.

Systemic Effect of UV Radiation on the Immune Response to Skin Cancers

Update of Research Results

Kripke and Fisher reported in 1976 that mice exposed repeatedly to UV radiation were systemically altered in that these animals were unable to reject UV-radiation-induced skin cancers transplanted to an unirradiated subcutaneous site. In contrast, these highly antigenic skin cancers were readily rejected by the immune system of unirradiated animals. This finding demonstrated that UV radiation had systemic, immunological consequences that previously were unsuspected, and it stimulated efforts to determine the nature and mechanisms of this phenomenon. Shortly thereafter it was found that the failure of UV-irradiated animals to reject these transplanted skin cancers was due to the formation of suppressor T lymphocytes that prevented the rejection response (Fisher and Kripke 1977, 1978; Spellman and Daynes 1977, 1978). Subsequent efforts have been directed mainly toward studies of the characteristics and mode of action of these suppressor cells (Thorn 1978, Daynes et al. 1979). An important recent advance in this area, however, was the direct demonstration that these suppressor T lymphocytes prevent not only the rejection of transplanted skin cancers, but also the destruction of primary skin cancers arising in UV-irradiated skin (Fisher and Kripke 1982). Furthermore, studies by De Gruijl and Van Der Leun (1982c) in hairless mice demonstrated that the systemic effect of UV radiation induced by irradiation of one site markedly accelerates the induction of skin cancers by subsequent irradiation of a second site.

A question of broader significance raised by these studies is whether this systemic effect of UV radiation can potentiate the growth or the induction of other types of cancer. Studies comparing the growth of cancers transplanted subcutaneously to UV-irradiated or untreated animals showed that growth of cancers generally is not accelerated in UV-irradiated mice unless the cancers are induced by UV radiation (Kripke 1981). Presumably, this is due to the fact that the UV-radiation-induced suppressor cells are specific for UV-induced tumors. An important exception to this generalization is the finding that a mouse melanoma that arose spontaneously grows more readily in UV-irradiated mice than in untreated animals (Kripke et al. 1979, Bowen and Brody 1983). It is not known whether this phenomenon is due to suppressor cells induced by UV radiation and thus depends on antigenic similarities between the melanoma cells and UV-radiation-induced skin cancers, or whether it represents some other systemic alteration by UV radiation (e.g., a hormonal, biochemical, or nutritional change) that is favorable for the proliferation of melanoma cells. In either case, however, the observation suggests a possible indirect role for UV radiation in the induction of melanomas.

In addition to the studies with transplanted cancers, a few experiments have been carried out to investigate the possible influence of the systemic effects of UV radiation on the occurrence of primary cancers of internal organs and on the induction of primary skin cancers at unirradiated sites by agents other than UV radiation. One study by Kripke and her co-workers (Kripke et al. 1979) showed that the incidence of virus-associated leukemias and mammary cancers in high-incidence strains of mice and chemical carcinogen-induced sarcomas is unaffected by exposure of mice to UV radiation. On the other hand, Ebbesen (1981) reported an increase in the incidence of spontaneous leukemias from 3 to 12 percent in mice exposed to low doses of UV radiation over a long period of time, and Roberts and Daynes (1980) reported that exposure of mice to UV radiation at one site accelerated the formation of epidermal cancers after repeated application of benzo(a)pyrene at a distant, nonexposed site. Clearly, additional information is needed in order to assess the potential of UV radiation to modify other forms of carcinogenesis.

Another question of considerable interest in this area is how exposure of the skin to UV radiation is translated into an immunological alteration involving the formation of suppressor cells that are specific for the antigens expressed on UV-radiation-induced skin cancers. One possibility is suggested by the studies on Langerhans cells and contact sensitizing antigens. New antigens that occur on UV-irradiated skin or on the tumor cells themselves might behave like the contact sensitizing antigens applied to UV-irradiated skin and induce suppressor cells because of a fault in antigen presentation by Langerhans cells. Another possibility is suggested by the finding described below that higher doses of UV radiation also can induce suppressor cells to contact sensitizers that are applied on unexposed skin, by an indirect mechanism that is not fully understood (see Figure 8-1). Because of technical considerations, it is much easier to analyze immunological pathways using contact sensitizers than it is using skin cancer antigens. For this reason all recent studies on the mechanisms of systemic suppression by UV radiation have focused on the systemic suppression of CHS, rather than on the induction of the skin-cancer-associated suppressor cells.

Wavelength and Dose Considerations

Wavelengths in the UV-B region also are implicated in this immunological alteration. The most effective wavelengths for impairing tumor rejection lie within the range of 275 to 315 nm. This result was determined using plastic filters to attenuate various wavebands of radiation from fluorescent sunlamps (DeFabo and Kripke 1980). Detailed information on the action spectrum for this effect is not available, but based on a single observation (Lill 1983), it appears that 254-nm (UV-C) radiation also is capable of producing this effect, although with lesser efficiency.

A seemingly contradictory result was reported by Gurish et al. (1981) in studies employing a commercial sunscreen preparation. Topical treatment of mice with the sunscreen prior to each irradiation with a fluorescent sunlamp eliminated all evidence of skin damage, but did not prevent the induction of immunosuppression by UV radiation. This result was interpreted as indicating

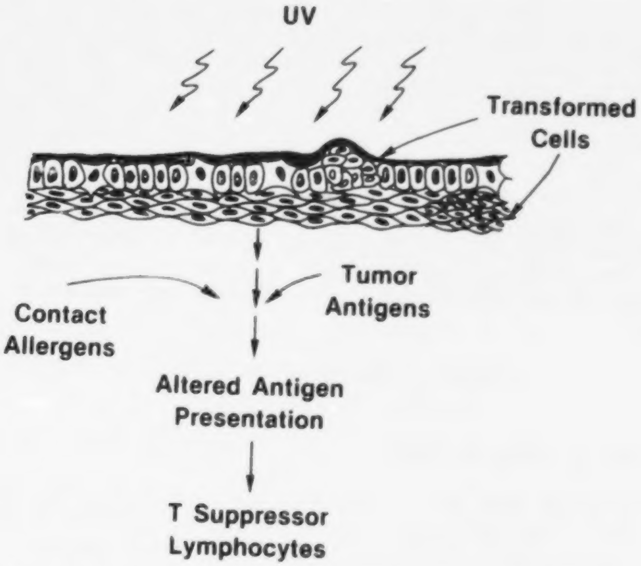


FIGURE 8-1 Model for the multiple effects of UV radiation on skin, leading to formation of suppressor lymphocytes. SOURCE: Reprinted, with permission, from Kripke (1983) Immunobiology of photocarcinogenesis *in* The Effect of Ultraviolet Radiation on the Immune System, Albuquerque, N.M., © 1983 Johnson & Johnson Baby Products Co.

that longer UV wavelengths in the range between 320 and 400 nm (UV-A) were responsible for the induction of tumor susceptibility. However, in view of the studies with optical filters, it is more likely that sufficient UV-B radiation penetrated the sunscreen to produce the immunosuppression. These observations suggest that the action spectra for erythema and systemic immunosuppression are different, and that using a sunscreen to prevent sunburn may not protect against immunological changes.

Compared with the doses of UV-B radiation used to affect Langerhans cells, the doses required to suppress tumor rejection are quite high and approach a carcinogenic dose. Roughly 1 to 2 x 10^5 J/m^2 of UV-B radiation are needed to produce this effect. Although this dose is quite high compared with a single ordinary human exposure to UV radiation from sunlight, the effect has been shown in mice to be cumulative over long periods of time (DeFabo and Kripke 1979). For example, 12 exposures of 18 kJ/m^2 each, given over a 4-week period, produce the same effect as a single exposure of 216 kJ/m^2 of UV-B. The changes produced in mice by UV radiation therefore apparently are long lasting and are not readily repaired. Furthermore, only the total dose of UV radiation is important; the rate of delivery and the time interval over which the dose is given have little influence on the induction of immunosuppression. The implication of this finding for humans is that short, repeated exposures to UV radiation over a long period of time may be just as effective for producing systemic immunological alterations as a single, long exposure.

Systemic Effects of UV Radiation on Other Immune Responses

Update of Research Results

The finding that UV-irradiated mice were unable to reject UV-radiation-induced skin cancers led to studies on the ability of these animals to carry out other immune responses (reviewed in Kripke 1981). These early studies demonstrated that many immune responses, such as antibody formation, allograft rejection, and inflammation at unexposed sites are unaffected by UV irradiation of the host. However, as illustrated in Figure 8-2, the CHS response to chemicals applied to unirradiated skin is impaired (Jessup et al. 1978). In normal mice, application of the contact sensitizing agent trinitrochlorobenzene to shaved abdominal skin induces a cell-mediated immune response. A second exposure to TNCB on the ears several days later elicits an allergic reaction characterized by swelling of the ear 24 hours later (contact hypersensitivity reaction). However, if the mice are first exposed to UV-B radiation on shaved dorsal skin several days before application of TNCB to unirradiated abdominal skin, no allergic reaction can be elicited, and suppressor cells can be found in the spleen of the animals.

The main difference between this phenomenon and the suppression of CHS by application of the chemical to irradiated skin is the dose of radiation required: approximately 100 times more UV radiation is required to induce systemic suppression of CHS than is needed to produce local suppression. The systemic suppression of CHS also is associated with the production of antigen-

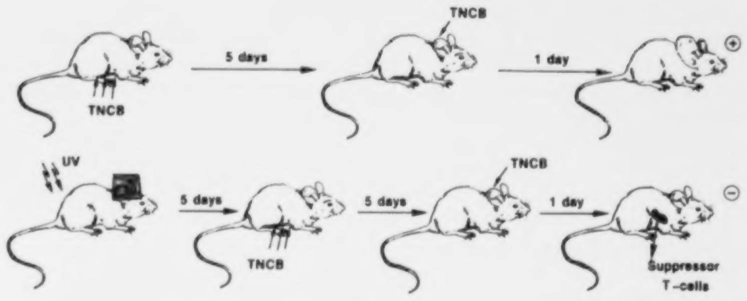


FIGURE 8-2 Systemic suppression of contact hypersensitivity by exposure of mice to UV-B radiation.

specific suppressor T lymphocytes (Noonan et al. 1981a), which again are thought to result from an alteration in antigen presentation, in this case by macrophages of the spleen (Greene et al. 1979, Noonan et al. 1981b).

How UV irradiation of the skin affects antigen presentation by cells in the spleen remains one of the unsolved mysteries in this area. Recent data on the wavelength dependence of this immunosuppression suggest that it is not due to direct irradiation of blood-borne macrophages (monocytes) circulating through capillaries in the skin (DeFabo and Noonan 1983). In addition, this systemic immunosuppression appears not to be related to the effects of UV radiation on Langerhans cells, based on differences in the wavelengths of UV radiation that mediate the two effects (Noonan et al. 1982). There are two remaining hypotheses. One is that a soluble mediator is formed in the skin following UV irradiation and that this photoproduct alters antigen presentation in the spleen. Based on the action spectrum for this effect, DeFabo and Noonan (1983) suggest that urocanic acid, a compound present in skin, is a possible candidate for such a mediator. The other hypothesis is that cellular injury in the skin following UV irradiation serves as a stimulus for macrophages to leave the spleen and accumulate at the site of damage, thereby being unavailable to carry out their antigen-presentation function. Circumstantial evidence supporting this hypothesis is that cells with antigen-presenting activity can be recovered from lymph nodes draining the irradiated skin at a time when they are absent from the spleen (Gurish et al. 1982) and that changes in the homing pattern of lymphocytes occur after UV irradiation of the skin (Spangrude et al. 1983). Furthermore, an agent that causes cellular injury by a different mechanism than UV-B radiation also was found to produce systemic suppression of CHS and to induce suppressor cells (Kripke et al. 1983).

In addition to studies of the mechanism of systemic suppression by UV radiation, two recent observations have been made relating to the generality of this phenomenon. One is that the systemic suppression of CHS and the induction of suppressor cells occur in the guinea pig as well as in the mouse (Morison 1983). This finding is important because guinea pig skin has many more similarities to human skin than does mouse skin in terms of optical and immunological properties. Thus, the likelihood that similar effects of UV radiation can occur in humans is increased by this result. Second, a preliminary report indicates that this form of immunosuppression is produced in mice following exposure to natural sunlight, as well as to artificial sources of UV radiation (Morison 1983).

Wavelength and Dose Considerations

The wavelength dependence for this phenomenon has been studied in detail, using very narrow wavebands of radiation throughout the UV-C and UV-B regions (250 to 320 nm). An action spectrum has been determined for the effect, which shows that wavelengths throughout this range can cause immunosuppression. The most efficient wavelengths are in the range from 260 to 270 nm, but 290-nm radiation is also highly effective (DeFabo and Noonan 1983). The action spectrum clearly differs from that for erythema, because the wavelengths that are most effective in producing immunosuppression are not the same as those that are most effective in producing sunburn and gross injury of the skin. It also appears to differ from the action spectrum for altering Langerhans cells (Noonan et al. 1982) and local suppression of CHS (Elmets et al. 1983). However, it should be emphasized that all of these effects are mediated by wavelengths in the UV-B region. The fact that sunlight can suppress CHS in mice suggests that sufficient environmental UV-B is present under current conditions to produce systemic immunosuppression.

As mentioned earlier, approximately 100 times more UV radiation is required to produce systemic suppression of

CHS than to produce local suppression. Between 2 and 4 x 10^4 J/m^2 are needed, but this dose still is considerably less than that required to suppress tumor rejection (1 to 2 x 10^5 J/m^2). The difference in dose requirement between suppression of tumor rejection and systemic suppression of CHS is most likely due to the fact that both the suppressor pathway must be activated and antigenic changes must be produced in skin in order to suppress tumor rejection (Noonan et al. 1981a). Thus, the greater dose of UV radiation required to suppress tumor rejection may be due to this additional production of antigenic changes.

As in the case of suppression of tumor rejection, the systemic suppression of CHS by UV radiation is cumulative. That is, multiple exposures to small doses (9 kJ/m^2) appear to be just as effective as a single exposure to a large dose (54 kJ/m^2) (Noonan et al. 1981a).

There are several questions that remain to be answered. What, for example, is the exact sequence of events leading to systemic immunosuppression? A second concerns the extent of this effect: that is, are there other immunological responses that are impaired following UV radiation? Perhaps most important is the question of the relationship between this form of immunosuppression and the suppression of tumor rejection. Although there are similarities between the two phenomena in terms of wavelength dependence, lack of repair, and the production of antigen-specific suppressor T lymphocytes (Noonan et al. 1981a), there is as yet no direct evidence that they are related. Thus, it is possible that suppression of tumor rejection is due to a combination of the two mechanisms described for suppression of CHS, or to another, still-unidentified pathway.

Antigenic Changes Induced by UV Radiation

The fact that most skin cancers induced in mice by UV radiation are immunologically rejected by unirradiated syngeneic (genetically identical) mice indicates that these cancers are highly antigenic. Although many skin cancers induced in mice by other carcinogens also are antigenic, they rarely have sufficient antigenicity to induce immunological rejection. Thus, the UV-radiation-induced skin cancers represent a unique class of experimental cancers from an immunological point of view. Another interesting feature of these cancers is that they appear to have more than one type of antigen. This conclusion is based on the finding that UV-induced cancers, like those induced by chemical carcinogens, have individually specific tumor rejection antigens (Kripke 1981). This characteristic dictates that the immune response that develops during the rejection of one skin cancer is specific only for that cancer, and does not recognize other UV-induced tumors. On the other hand, the suppressor cells present in UV-irradiated mice prevent the rejection of all UV-induced skin cancers, implying that a common, UV-associated antigen is also present.

The relationships among these types of antigens, UV irradiation, and the transforming event are currently unknown. It is thought that at least some of the antigenic changes exhibited by these skin cancer cells are induced by the UV radiation itself and are not merely a peculiar feature of the cells in which these cancers arise. This idea is based on two lines of evidence. First, skin cancers induced in mice by psoralen, a chemical photosensitizer, plus UV-A radiation (320 to 400 nm) appear to arise in the same types of cells as those induced by UV-B radiation, but they are not highly antigenic (Kripke et al. 1983). Second, in vitro transformation of mouse epidermal cells with UV-B radiation also produces cancers that are highly antigenic (Ananthaswamy and Kripke 1981). These studies are interpreted as indicating that UV radiation causes antigenic changes in cells that are exposed directly to the radiation. It is not clear whether these changes are related to the neoplastic transformation of these cells into cancer cells, or whether they are independent of transformation.

Little else is known about the origin and nature of these antigens. A recent study suggested that they may be present in UV-irradiated skin prior to the appearance of recognizable cancers (Palaszynski and Kripke 1983). Grafting UV-irradiated, but not normal skin to unirradiated animals decreased the ability of the recipients to reject transplants of UV-induced skin cancers. This result suggests that UV-induced antigens may be present on irradiated skin and that these antigens can induce suppression of tumor rejection; however, other possible interpretations of this result have not yet been ruled out.

There is also little information available on the dose and wavelengths of UV radiation that lead to the antigenic changes. A recent study by Lill (1983) demonstrated that skin cancers induced in mice by UV-C radiation (at 254 nm) have antigenic properties similar to those induced by wavelengths in the UV-B region. No information is available on the doses of radiation required to produce antigenic changes due to the fact that there is no direct way of detecting or measuring the antigenic changes during the course of irradiation. Currently, the antigens can be detected only by transplantation tests, after neoplastic transformation has occurred and a visible tumor is present. The lack of an in vitro assay for UV-associated antigenic changes is a major obstacle to progress in this area and precludes a search for comparable antigenic changes in human skin.

STUDIES ON HUMANS

In recent years interest in the possible immunological consequences of exposure of humans to UV radiation has been stimulated by two factors. One is the discovery of the extensive interactions between UV-B radiation and the immune system in experimental animals; the other is the success of UV radiation in the treatment of certain skin diseases thought to have an immunological basis. Over the last decade there have been isolated observations indicating that sun-damaged skin is deficient in immunological reactivity, but the mechanism of these aberrations was not clear (reviewed in Morison 1983). More recent studies have focused on specific questions raised from the experiments on animals. These questions include whether Langerhans cells in human skin are affected by exposure to UV radiation and/or natural sunlight, and whether systemic suppression of immune responses can occur in humans exposed to environmental sources of UV radiation.

Direct Effects of UV Radiation on Langerhans Cells in Human Skin

There are several studies demonstrating that human Langerhans cells are quite sensitive to damage by UV radiation. Aberer et al. (1981) reported that moderate doses of UV-B or UV-A radiation from sunlamps could alter the morphology and surface markers of Langerhans cells in human skin. Scheibner et al. (1983) have recently surveyed the number and body distribution of Langerhans cells in the skin of human subjects at the time of autopsy. They found that skin from sun-exposed parts of the body had substantially fewer Langerhans cells than skin from protected areas. In addition, the cells that were present were unevenly distributed in the irradiated skin. This study concurs with those of Zelickson and Mottaz (1970) and Gilchrest et al. (1982), which showed that the number of Langerhans cells was reduced following experimental exposure of humans to sunlight. More importantly, it demonstrates that long-term natural exposure to sunlight significantly alters these immunological cells. The functional significance of these changes in Langerhans cells currently can only be surmised, but it is likely that they play a role in the immunological alterations described below.

Effects of UV Radiation on Other Lymphoid Cells and on Immune Responses

The first suggestion that there might be systemic immunological changes in humans exposed to UV-B radiation came from the work of Morison et al. (1979). This study showed that a single dose of UV-B radiation sufficient to cause a mild sunburn in normal subjects decreased the viability of their circulating lymphocytes and altered the activity of these cells in an in vitro test. These changes persisted up to 24 hours after the exposure to UV-B radiation. Recently, more extensive studies carried out in Australia by Hersey and colleagues demonstrate that there are functional alterations in certain immune responses after exposure to UV radiation or sunlight, in addition to changes in the number and proportions of various lymphocyte subpopulations. In these studies, healthy human volunteers were given a 2-week course of exposures to solarium radiation, containing both UV-A and UV-B wavelengths, in a commercial tanning salon (Hersey et al. 1983b), or 12 1-hour exposures to sunlight over a 2-week period (Hersey et al. 1983a). When dinitrochlorobenzene was applied to skin that had been exposed to solarium radiation, the CHS response was impaired. This test was not performed in the study with sunlight, but in both studies the number and activity of suppressor lymphocytes was increased, and the number of helper lymphocytes was reduced after irradiation. Some of these changes persisted in the subjects for at least 2 weeks after the end of the treatment period.

Many questions remain to be resolved in this area. For example, it has not been proven formally that these effects of radiation on the immune system of human subjects are due to wavelengths in the UV-B region, although this is almost certainly the case. Also, the extent of these immunological perturbations is still unknown. Most importantly, the significance of these changes in infectious diseases, wound healing, and the pathogenesis of skin cancers and cutaneous metastases is not yet known. Nonetheless, it is clear that UV radiation can alter immune function in humans, and thus far these alterations parallel those described more fully in experimental animals.

IMPLICATIONS OF INCREASING UV-B RADIATION

Based on the preceding review, it is quite likely that increasing the exposure to solar UV-B radiation will increase the magnitude and perhaps the duration of the immunological alterations that have been identified in human subjects. Studies with animals show that there is a direct and predictable relationship between the dose of UV-B radiation and the magnitude of certain immunological effects, including morphological alterations in Langerhans cells, systemic suppression of contact hypersensitivity reactions, and inhibition of the rejection of skin cancers. Although the dose-response relationships may not be identical in humans and in rodents because of differences in DNA repair, skin optics, etc., it is almost certain that any increase in the dose of UV radiation within this biologically active range of wavelengths will increase immunological perturbations.

The report that a commercial sunscreen preparation can prevent sunburn in mice without preventing suppression of skin cancer rejection is quite provocative. If the same situation occurs in humans, it may signify that increases in the use of sunscreens may not compensate for all of the immunological effects of increases in UV-B radiation. Clearly, additional information on this topic is required, both in animals and in human subjects.

The most significant implication of these immunological changes is the possibility that certain skin diseases, including skin cancers, may increase as a result of increasing exposure to UV-B radiation. This is not to say that the calculated risk of developing sunlight-associated skin cancers will increase because of the discovery that immune suppression is induced by UV-B radiation. The relationships between UV-B exposure and the incidence of nonmelanoma skin cancer on sun-exposed parts of the body are based on epidemiological data and thus include the effects of all mechanisms. The finding of UV-B-induced immune suppression does not alter these epidemiological data, but rather may help to explain them. On the other hand, the discovery of UV-B-induced immunological alterations raises the possibility that there are adverse effects of UV-B radiation on human health in addition to the induction of skin cancer. For example, it has been suggested that immunosuppression induced by UV radiation might be a factor in the ability of sunlight to activate herpes simplex virus infection. Studies in animals also suggest that immunosuppression might contribute to the pathogenesis of malignant melanoma and to skin cancers that occur on parts of the body not exposed to the sun. Although there is no direct evidence in humans to support these conjectures, it is clear that there is a strong interrelationship between the immune system and resistance to viral infection, and between the immune system and skin cancer in humans. A striking example of the latter association is found in the very high incidence of skin cancer, as well as lymphoid cancers, in patients receiving immunosuppressive therapy following organ transplantation (Koranda et al. 1974, Marshall 1974, Hoxtell et al. 1977). This observation suggests that immunosuppressive agents may weaken an important defense mechanism that helps to eliminate cancer cells in the skin. Obviously, in this area of investigation it is too early to be able to make quantitative predictions about the effects of increases in UV-B radiation on immune responses or predictions about the significance of these immunological alterations for human health. These assessments require more information than is currently available. However, it seems clear that concerns about the possible immunological consequences of exposure to sunlight are well-founded and worthy of additional investigation, particularly with regard to their possible effects on skin diseases, malignant melanoma, and wound healing.

RESEARCH RECOMMENDATIONS

- Investigations of the mechanisms in animals by which UV radiation affects immunological processes must be continued.

- The extent of the immunological changes that occur in humans exposed to sunlight should be determined.
- The wavelength dependence of the immunological alterations produced in humans by sunlight exposure needs to be established and the dose-response relationships for these effects need to be defined.
- The relevance of the immunological alterations induced by UV radiation for human skin cancers and other diseases in humans must be determined.

9

Nonmelanoma Skin Cancers in Humans

NRC (1982) summarized the abundant evidence that ozone depletion will increase UV-B flux reaching the Earth's surface, and that this increase will result in an increased incidence of basal cell carcinoma and squamous cell carcinoma. The percentage increase in nonmelanoma skin cancer occurring as a result of a 1 percent increase in UV-B flux is commonly referred to as the biologic amplification factor (BAF). Accurately establishing the magnitude of the BAF is central to predicting the changes in incidence of basal cell and squamous cell cancers expected as a consequence of changes in UV-B insolation accompanying reductions in stratospheric ozone or resulting from changes in exposure due to other factors.

As reviewed in earlier reports, a number of different models have been used to relate chronic UV exposure to skin cancer risk and to estimate the amplification factor. Using data from the Third Cancer Survey and R-B meter readings, Fears and Scotto (1983) predicted the amplification factor using two mathematical models, one a simple power function and the other a simple exponential function. According to the power model, a 30 percent increase in UV-B exposure would increase the incidence of skin cancer by 60 percent in males and 45 percent in females. According to their exponential model, the amplification factor for increased UV-B varies substantially between geographic areas, with the amplification factor for nonmelanoma skin cancer being greater in areas of higher UV-B insolation (Fears and Scotto 1983).

These authors have also refined their simple power function model to consider separately the effect of increased UV-B on basal cell and squamous cell carcinomas. Their model predicts that a 1 percent increase in UV-B will have a greater effect on the risk of squamous cell carcinoma than on that for basal cell carcinoma, with the amplification factor for squamous cell equal to 2 in more northern latitudes and 4 in areas of the United States receiving higher UV dose. Their estimates for the amplification factor for basal cell carcinoma are approximately half those for squamous cell carcinoma, and they predict that the amplification is slightly higher for men than for women (Scotto et al. 1983).

Rundel (1983b) applied a different mathematical approach (the nonlinear least-squares technique) to the same data that Scotto, Fears, and Fraumeni (1983) used, and predicted that a 1 percent ozone layer depletion would eventually lead to a 1.7 percent increase in basal cell carcinoma incidence and a 2.3 percent increase in squamous cell carcinoma incidence. He also predicted a greater incidence among males and among populations living in areas of higher UV radiation, and suggested that the sun-seeking behavior and the ethnicity of a population may, in part, account for deviations from the model.

Rundel and Nachtwey (1983) projected the increase in nonmelanoma skin cancer incidence due to ozone depletion under five different depletion circumstances ranging from a 2.5 percent decrease to an eventual 30 percent ozone depletion. Using Rundel's model, which employs relatively modest amplification factors, the authors show that an eventual 30 percent ozone depletion would result in a doubling of skin cancer by the year 2300. The authors do not present a sensitivity analysis for their amplification factor, or incorporate changes in life expectancy, geographic residence, and exposure habits into their models.

De Gruijl and Van Der Leun (1980) developed a model based on animal experiments, which tries to take into account exposure habits and individual susceptibilities in a population. Their model suggests an amplification factor of 4, which is slightly higher than that advanced by Fears or Rundel. However, in view of the uncertainties associated with the several assumptions that underlie these models, the amplification factors predicted by the three models are in all likelihood statistically indistinguishable.

These models do not adequately account for three possibly important factors: (1) the aging of the U.S. population, (2) the shift of populations to the South and Southwest, and (3) the increased leisure time projected for the coming decades. Independent of any increases in UV-B insolation, each of these social-demographic factors is likely to increase the total dose of UV-B to which individuals are exposed in their lifetimes and the consequent incidence of nonmelanoma skin cancer in the United States. Since the percentage increase in squamous cell carcinoma incidence for each percentage increase in total UV-B exposure is considered to be greater than that for basal cell carcinoma, each of these trends suggests that independent of changes in UV-B insolation, squamous cell carcinoma incidence is likely to increase at a higher rate than basal cell carcinoma incidence. Therefore, the simultaneous occurrence of increased UV-B insolation and the above-noted social and demographic changes may lead in the coming decades to a substantially greater increase in the incidence of squamous cell carcinoma, the clinically more serious nonmelanoma skin cancer than is predicted from models used in the past. As noted above, all models seem to agree that the amplification factor is higher in areas of higher UV flux.

In mice, De Gruijl and his co-workers (1983) have demonstrated that both dose per day and latency may be important in determining the cancer risk for a given cumulative UV dose. Obviously people spending more leisure time outdoors in southern areas of high UV-B flux will receive a greater cumulative dose, and the aging (i.e., increasing life expectancy) of this population may well provide a latency period sufficient for promotion of the original UV-initiated nonmelanoma skin cancer.

De Gruijl and Van Der Leun (1982a) also demonstrated that some of the variations in risk as a function of flux may be the result of adaptive phenomena, which, in the mouse, includes epidermal thickening. Such may not be the case for humans in whom older, sun-exposed skin tends to be thinner than young exposed skin and may not undergo the same hyperphasia in response to UV-B. If this is true, then for a given increase in UV-B insolation, we can expect that the effective dose of UV-B reaching the skin's basal cell layer will increase relatively more in older than in younger persons. These factors suggest that the eventual increase in the lifetime risk of nonmelanoma skin cancer will be greater than that predicted by the current models for the amplification factor.

Another important research area that has bearing on the effect of ozone depletion is the characterization of persons at higher risk for nonmelanoma skin cancer. Previous work by Tannenbaum et al. (1976) and Jung et al. (1979) indicated that patients exhibiting prolonged UV-B-induced erythema were at higher risk of nonmelanoma skin cancer, independent of other attributes such as fair skin, poor tanning, or Celtic ancestry. More recent work by Gregg and Mansbridge (1982) showed that nonmelanoma skin cancer patients had nearly twice the level of basal cell tritiated thymidine labeling than their own family members or members of families without a history of skin cancer. These authors were unable to demonstrate a difference in DNA repair in UV-B response between persons with and without skin cancer, and their data await confirmation from other investigators. Nevertheless, the availability of a simple means to differentiate high-risk persons would be a useful tool for the analysis of increased cancer incidence due to ozone depletion.

RESEARCH RECOMMENDATIONS

- Predictions of basal cell carcinoma and squamous cell carcinoma incidence based on epidemiological data must take into account social and demographic factors as well as changes in UV-B insolation.
- Prospective studies of patients undergoing various forms of phototherapy could be helpful in identifying patient characteristics associated with nonmelanoma skin cancer risk and in determining the relative importance of different wavebands to human skin cancer.
- Periodic determination of squamous cell carcinoma and basal cell carcinoma incidence at a variety of geographic sites should be performed.
- Measurement of annual UV-B insolation at those geographic sites should be continued.

10

Malignant Melanoma in Humans

Malignant melanoma of the skin (Figure 10-1 [color plate]) is caused by cancerous proliferation of melanocytes. Melanocytes are those cells (Figure 10-2) that produce the brown pigment, melanin, which is responsible for the principal differences in the colors of the various races of man. Also, melanin is the pigment that results in protective tanning after exposure to UV radiation. Since malignant melanomas arise from these melanin-producing cells, they are usually deeply pigmented with characteristic tan, brown, black, and blue colors.

Most malignant melanomas begin as a proliferation of neoplastic melanocytes at the junction of the epidermis and the dermis. Often the proliferating cells spread parallel to the surface of the skin for some years before they invade the dermis or subcutis to various depths. The deeper the level of penetration or the thicker the malignant melanoma, the poorer the prognosis (Clark et al. 1969, Breslow 1970).

Malignant melanoma can take several different forms. Although these cancers are relatively uncommon, most are quite serious diseases. Evidence exists both to support and to refute the hypothesis that incidence of malignant melanoma is related to exposure to sunlight. In some types, such as lentigo maligna melanoma and in melanoma arising in patients with xeroderma pigmentosum, the relationship to sunlight is relatively clear. In other cases the evidence is circumstantial or is inconsistent with an etiology involving sunlight. It appears likely that as we learn more about the different types of malignant melanoma (see, for example, Chapters 8 and 12), we shall come to understand which ones involve a relationship with sunlight and which do not.

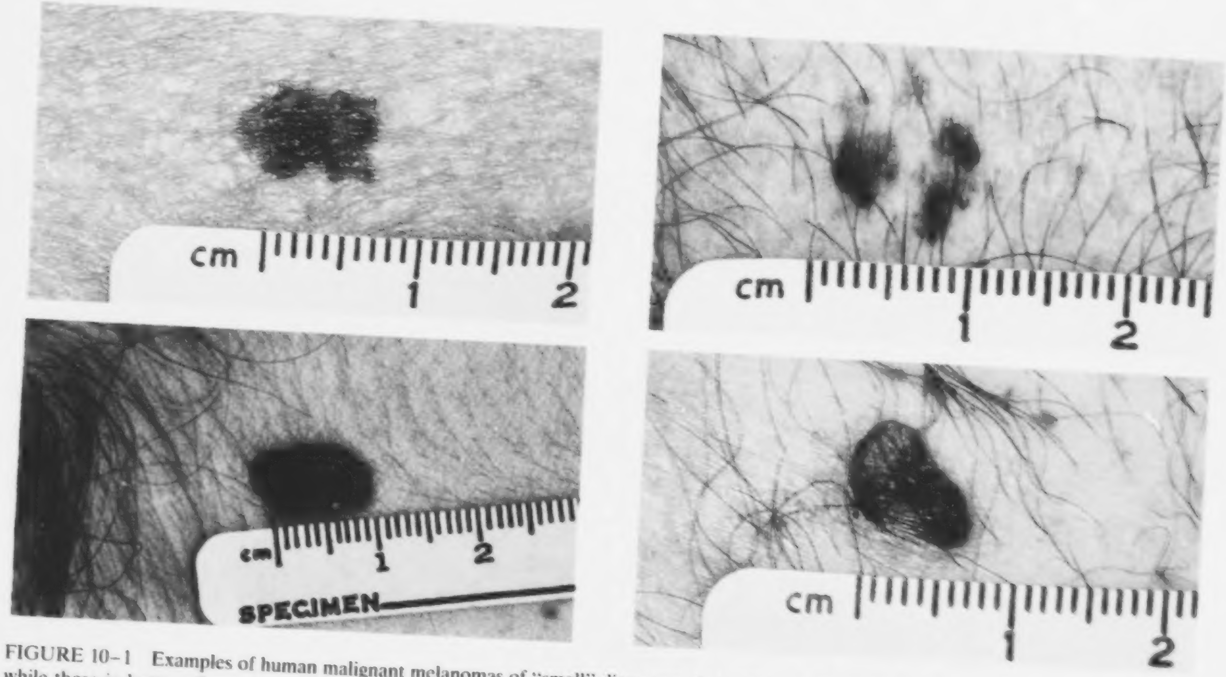


FIGURE 10-1 Examples of human malignant melanomas of "small" diameters. In top figures the malignant melanomas are Level I (in situ), while those in bottom figures are Level III. The melanomas in bottom figures (left and right) are 1.4 and 0.9 mm thick, respectively.

SOURCE: Reprinted, with permission, from Kopf et al. (1982b). Journal of Dermatologic Surgery and Oncology 8(9):765–770. © 1982. The Journal of Dermatologic Surgery and Oncology, Inc.

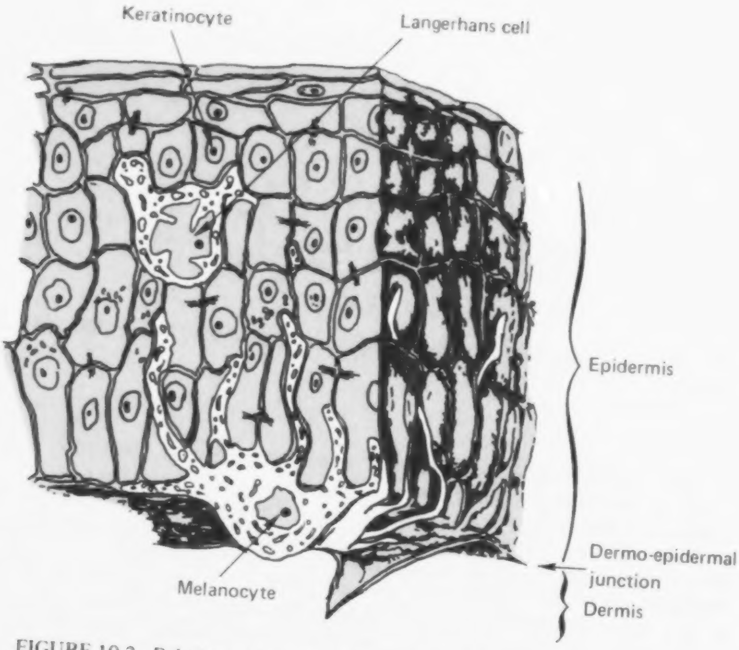


FIGURE 10-2 Relation of a basal melanocyte, "high-level" Langerhans cell, and keratinocytes in mammalian epidermis. Melanocytes produce melanin (the small dark granules), which is injected into keratinocytes where the pigment serves as a sunscreen. SOURCE: Adapted from Quevedo (1969).

In this chapter we first describe data on incidence and mortality in humans that, for the most part, do not distinguish among the types of malignant melanoma. We then describe the evidence both for and against a relationship with sunlight. Following a brief section on malignant melanoma in animals, we discuss the implications of current understanding in the context of protecting stratospheric ozone. Finally, several recommendations for further research are presented.

INCIDENCE AND MORTALITY DATA

The American Cancer Society has predicted that 17,400 people in the United States will develop malignant melanoma in 1983, and that approximately 5,200 people will die of this disease in that year (Silverberg and Lubera 1983).

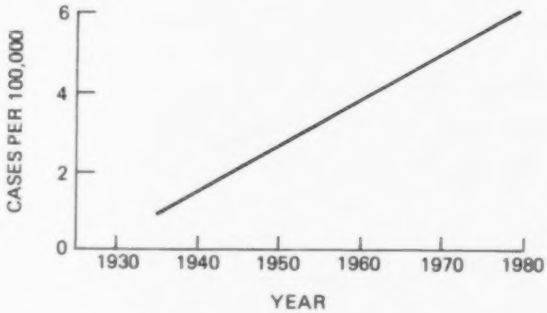


FIGURE 10-3 Incidence of malignant melanoma in the United States, 1935-1980. SOURCE: Kopf et al. (1982a).

The incidence of malignant melanoma in the United States has been rising consistently during the last 50 years. Figure 10-3 shows that the incidence of this cancer was approximately 1 per 100,000 population in the mid-1930s but by 1980 had risen to 6 per 100,000 population. In 1930 the probability that an individual would develop malignant melanoma during an average life span was 1 in 1,500. By 1950 the probability increased to 1 in 600; by 1980, 1 in 250; and, if the current rate of increase continues, 1 in 150 individuals born in the year 2000 and living a full life span will develop malignant melanoma of the skin. In New South Wales, Australia, the incidence in 1974 was such that approximately 1 in 66 people residing there will develop malignant melanoma by age 74 (Armstrong et al. 1982). In many countries the incidence of malignant melanoma is doubling every 10 to 14 years (Muir and Nectoux 1982). In Scandinavia the incidence of malignant melanoma doubled in just 7 years (Magnus 1977). If this trend obtains into the future, by the end of this century malignant melanoma in Norway will be more common than malignancies of the breast and lung (MacKie 1982). The fact that the incidence of nonmelanoma cancers of the skin is rising as fast or faster than that of malignant melanoma is another observation that links the two types of cutaneous cancers (Lee 1982), but it does not necessarily imply a common etiology. As detailed in the NRC (1982) report and elsewhere in this report, substantial clinical, epidemiologic, and laboratory data implicate exposure to ultraviolet light (especially UV-B) as causal for nonmelanoma cancers of the skin.

The death rate from melanoma per 100,000 population in the United States has also been increasing steadily (Lee et al. 1979). During the past 30 years the mean annual percentage increase for women is 1.9 percent and for men is 3 percent. Thus, malignant melanoma of the skin has shown a larger increase in mortality rate in the United States since 1960 than cancer of any other site except lung. In many other countries, mortality from malignant melanoma is rising at a rate of 3 percent per year or more (Jensen and Bolander 1980) (Figure 10-4). These mortality data imply that the increasing incidence of malignant melanoma in humans is not merely the result of better diagnosis and reporting.

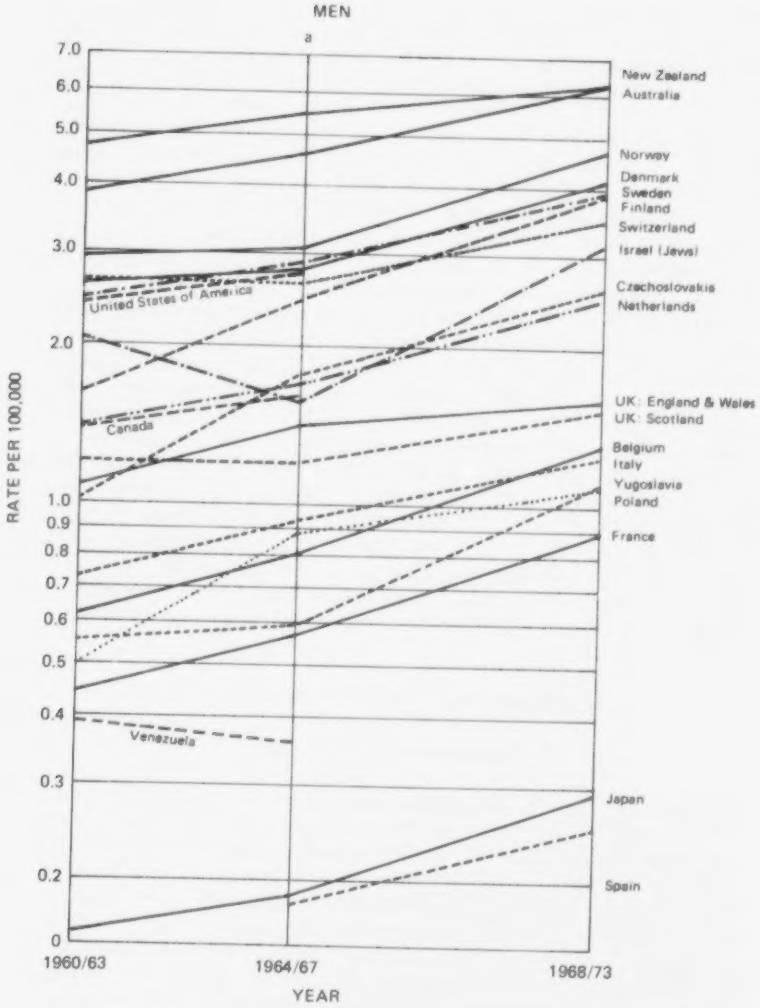
Figure 10-5 illustrates that in cohort analyses from Australia, each group of individuals born in a later decade had a higher death rate than cohorts born earlier (Holman et al. 1980a). Using cohort analyses, Day and Charnay (1982) and Teppo et al. (1978) reported similar data showing an inexorable increase in the incidence rates of malignant melanoma in Finland, and Magnus (1982b) found the same trend in Norway. Lee et al. (1979) have documented the rise in age-adjusted death rates in the United States in cohort studies. The universality of the cohort effect suggests an environmental factor as the cause of the constantly increasing incidence and mortality rates of malignant melanoma (Muir and Nectoux 1982).

EVIDENCE FOR THE ROLE OF SUNLIGHT

Exposure to Sunlight

Certain malignant melanomas are clearly related to sun exposure. Thus, lentigo maligna melanoma occurs almost exclusively on heavily sun-exposed areas of the face in elderly persons, and is the type of malignant melanoma most clearly related to cumulative sunlight exposure. Histologically, solar elastosis (an alteration of the connective tissue of the dermis caused by sun damage) is always found in this type of malignant melanoma. Also, malignant melanomas are frequently seen in people with xeroderma pigmentosum, in which there is a genetically determined defect in the repair of DNA damaged by UV radiation and a high risk of nonmelanoma cancers of the skin (Takebe et al. 1977, Kraemer 1980).

One of the most important observations that implicate sunlight in the pathogenesis of malignant melanoma of the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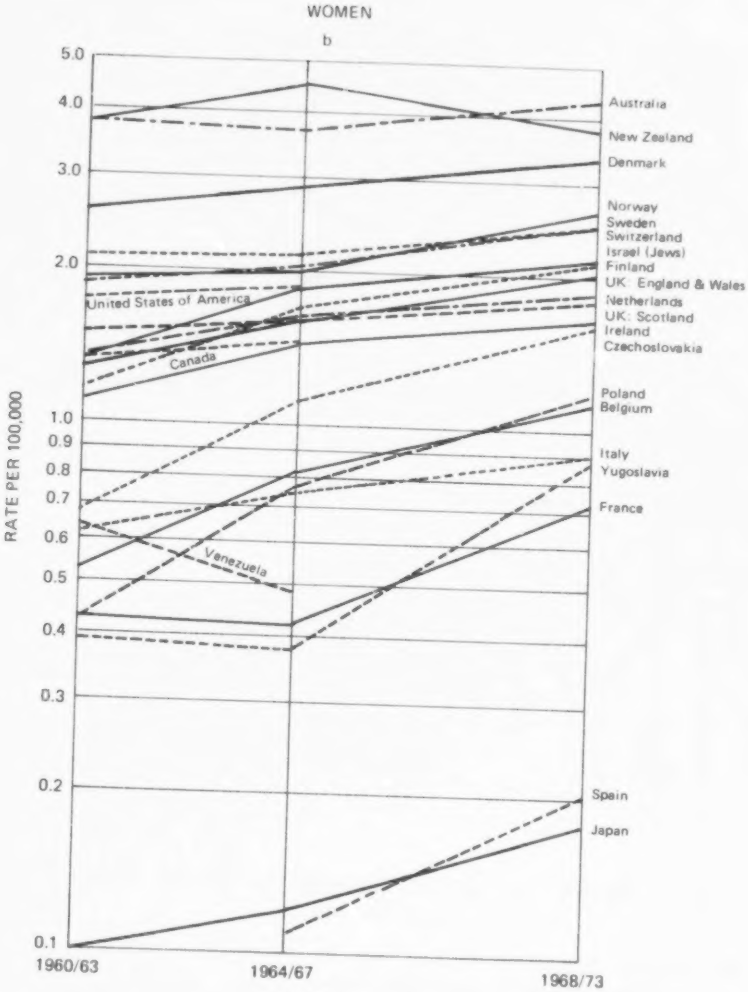


FIGURE 10-4 Trends in mortality from malignant melanoma of the skin, 1960-1973. Age-standardized truncated death rates per 100,000 for (a) men and (b) women. SOURCE: Jensen and Bolander (1980).

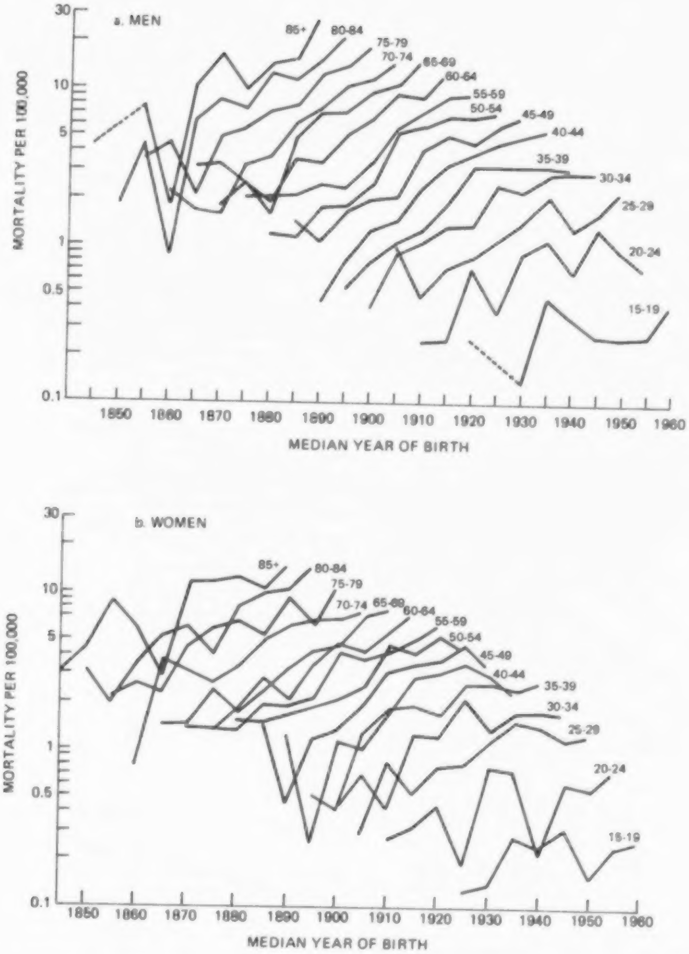


FIGURE 10-5 Annual mortality from malignant melanoma of the skin by age and year of birth in (a) Australian men and (b) Australian women. Mortality rate at any attained age increases for each later cohort (i.e., people born the same year). For example, persons when they attain the age of 55 to 59, if born in 1920, have a much higher death rate than those born in 1885 when they reach the age of 55 to 59. SOURCE: Holman et al. (1980a).

skin is epidemiologic data that demonstrate an inverse relationship between latitude and the incidence and mortality rates of malignant melanoma in Caucasians (Figure 10-6). That is, the closer to the equator (and therefore the greater the amount of sunlight), the greater are the incidence and mortality rates of malignant melanoma. In contrast, the incidence of malignant melanoma of the eye, which occurs primarily in the choroidal tissues near the retina, does not appear to be correlated with latitude (Scotto et al. 1976, Swerdlow 1983). One explanation for this is that the cornea absorbs UV radiation and therefore protects the choroid of the eye.

The highest incidence of malignant melanoma in the world is in sunny Queensland, Australia, where in 1977 the rate was 33 per 100,000 population (Little et al. 1980). The incidence of malignant melanoma in Tucson, Arizona, is almost as high--27 per 100,000 population (Schreiber et al. 1981). Southern Arizona has the unique combination of high average annual temperature, low average annual humidity, moderate altitude (2,400 ft), low atmospheric ozone, and more clear days, more sunlight, and less daytime cloudiness than other cities in the United States. The incidence of malignant melanoma in southern Arizona has quadrupled from 1969 to 1978 (from 6 to 27 per 100,000 population, age-standardized). The increased incidence of malignant melanoma in Arizona is seen only in Caucasians of Northern European descent but not in Latins of Spanish descent, blacks, or Indians. The incidence of malignant melanoma per 100,000 individuals has shown a progressive increase with increasing age (Young et al. 1981). Thus, with the increasing elderly population and tendency for Caucasians to migrate to the sunbelt areas such as Arizona, one can predict an even higher incidence and mortality rate for malignant melanoma in years to come even if there is no increase in insolation due to reductions in stratospheric ozone.

The length of residence of Caucasians in areas of high insolation such as Australia is directly correlated with the incidence of malignant melanoma (Armstrong et al. 1982, Dobson and Leeder 1982). Furthermore, a study of immigrants to Australia suggests that high sunlight exposure in childhood and adolescence contributes to the subsequent risk of malignant melanoma (Holman 1983). Also, the longer European immigrants live in Israel, the higher is their risk of developing malignant melanoma (Anaise et al. 1978, Katz et al. 1982).

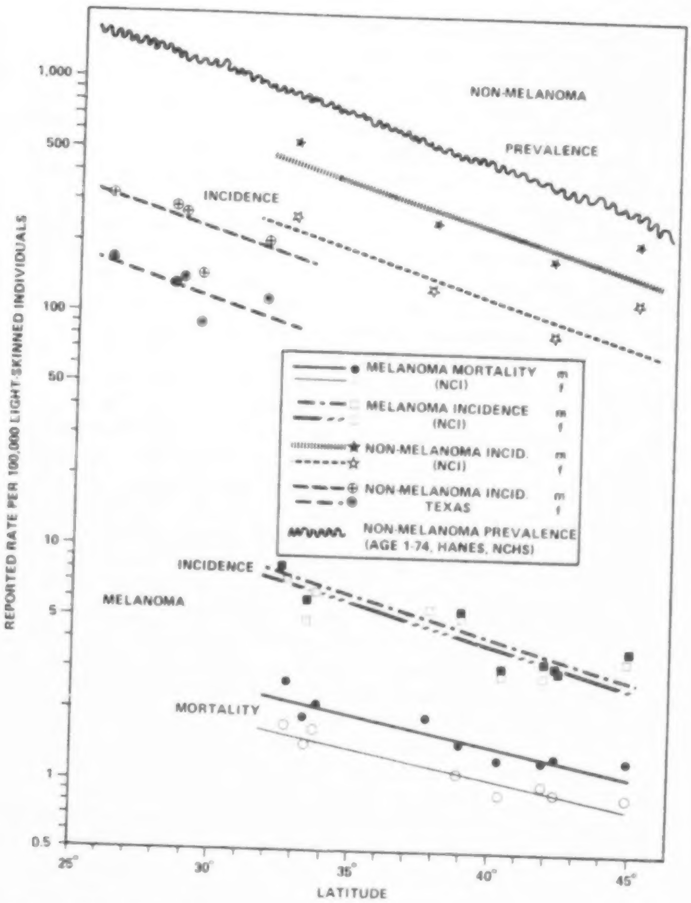


FIGURE 10-6 Annual age-adjusted rates for skin cancer by latitude. SOURCE: NRC (1975).

The mortality rate for malignant melanoma in the United States is also inversely proportional to latitude (Figure 10-6). A similar observation has been made in Australia (Holman et al. 1980a).

Some evidence suggests a relationship between intermittent, high-intensity bouts of exposure to sunlight and the induction of cutaneous malignant melanomas in humans (Fears et al. 1977, Wigle 1978, Swerdlow 1979, Holman et al. 1980b, Scotto and Nam 1980, Hinds et al. 1981, Lew et al., 1983). This theory of bursts of sunburn radiation has been invoked to explain the repeated observation that white collar urban workers are more susceptible to developing malignant melanoma than are blue collar workers (who tend to have chronic, rather than intermittent, solar exposure). Urbanites travel with greater frequency to sunny climates where they receive intense exposure to solar radiation episodically (Eklund and Malec 1978).

UV radiation from an artificial light is also involved with hyperplasia of melanocytes. For example, PUVA treatment (systemic administration of psoralen followed by exposure to UV-A) induces pigmented macules caused by proliferation of large, sometimes atypical, melanocytes (Rhodes et al. 1983b). Several cases of malignant melanomas appearing in patients treated with PUVA have recently been reported (Marx et al. 1983). Typically, the UV-A lamps also emit in the UV-B band, so it is not possible to distinguish between effects of UV-A and UV-B from these data.

Type of Skin

Malignant melanoma is predominantly a cutaneous cancer of Caucasians (Reintgen et al. 1982). The incidence of malignant melanoma is approximately 10 times greater for both white men and white women than for blacks (Young et al. 1981). Similarly, the mortality rate of malignant melanoma among whites is 5 times greater for both white men and white women than for blacks. There is in general an inverse correlation between incidence and the skin pigmentation of people in various countries in the world (Crombie 1979, Armstrong et al. 1982). Thus, the darker the race the lower is the incidence of malignant melanoma. These tendencies suggest that melanin, which decreases the transmission of a broad spectrum of electromagnetic radiation, may protect skin from sunlight-induced changes that lead to malignant transformation of melanocytes or contributes to their outgrowth. Indeed, it has been shown that transmittance of UV radiation through the skin is significantly less in blacks than in Caucasians (Figure 10-7). Having black skin is equivalent to wearing a sunscreen all the time (Kaidbey et al. 1979, Pathak and Fanselow 1983).

Gellin et al. (1969) have shown that, compared to an age- and sex-matched control population, individuals who

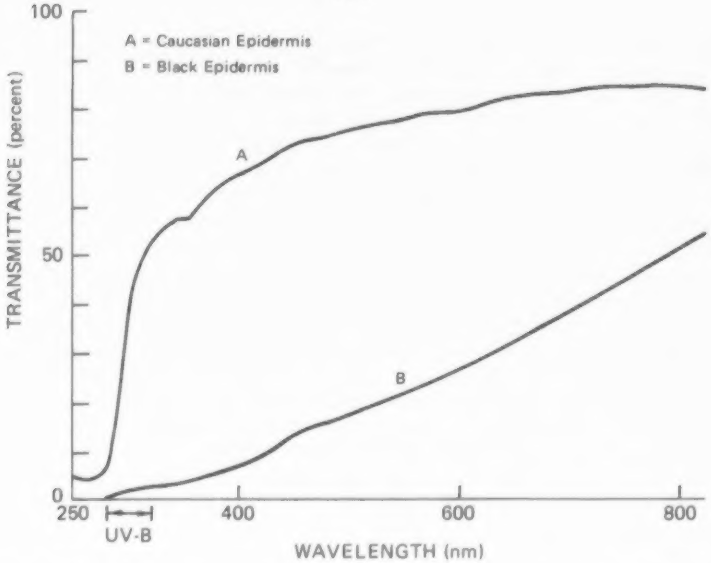


FIGURE 10-7 Transmittance of ultraviolet light by human epidermis. SOURCE: Parrish (1982).

develop malignant melanoma tend to have lighter complexions, lighter eye colors, lighter hair colors, and tan less readily but spend more time outdoors per day.

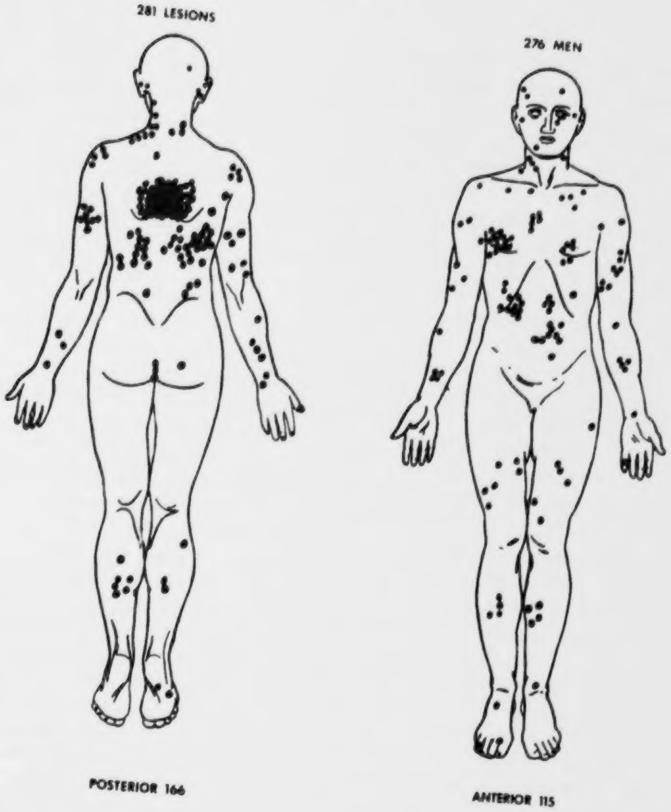
Caucasians can also be divided into "skin types" based on their sunburning and tanning abilities (Amblard et al. 1982). A greater percentage of melanoma patients have skin types I and II (i.e., those that tend to sunburn but not to tan) than control groups (Beitner et al. 1981). Individuals who develop malignant melanoma also sunburn more easily and have poorer delayed tanning ability than controls (Beitner et al. 1981). Furthermore, melanoma patients of all skin types have lower minimal erythema doses than controls have. Finally, Beitner et al. also found that the mean age of diagnosis increases with increasingly darker skin types. Jung et al. (1981) reported a significant prolongation of erythema following exposure of melanoma patients to UV radiation. In addition, these authors reported that the spontaneous and UV-C-induced sister-chromatid exchanges in peripheral blood leukocytes were more numerous in melanoma patients than in normal controls. Thus, there are data that suggest that malignant melanoma is correlated with increased susceptibility to UV-radiation-induced injury.

Anatomical Distribution

While basal cell and squamous cell carcinomas appear predominantly on exposed areas of the head and neck (Brodkin et al. 1969), malignant melanomas in Caucasians appear frequently on the back in both men and women and on the legs in women (Figure 10-8). A comparison of the distribution of nonmelanoma cancers of the skin with malignant melanomas in men and women is shown in Table 10-1. In the past few decades the principal sites of increase of malignant melanoma have been on the trunk of men and legs of women (Teppo et al. 1978, Teppo 1982). This distribution is consistent with the concept that these areas, as a result of changes in dress, are sites of increased exposure to sunlight. Interestingly the high prevalence of malignant melanomas of the legs in women is not seen in non-Caucasians (Hinds and Kolonel 1980). Several factors may combine to lead to an increased amount of sun exposure in these anatomical sites. Bathing suit styles have changed significantly since the turn of the century. In the early 1900s most of the body surface of women was covered by bathing suits, stockings, and bathing hats. Parasols were frequently carried at the beaches. Over the years both men's and women's swimsuits have progressively decreased in area so that less and less of the skin is protected. Indeed, Holman (1983) has shown that the more skimpy the bathing suit style worn, the higher is the risk of malignant melanoma. Also, synthetic fabrics, which are not woven as tightly as cottons and therefore have less sun-protective value, have largely replaced cottons (Welsh and Diffey 1981). These observations are consistent with the hypothesis that sunlight might have a direct transforming effect on melanocytes that are in the sun-exposed areas of the body. Alternatively the effect of sunlight may be to increase the number of target melanocytes (e.g., dysplastic nevi), which in turn are transformed by some unidentified carcinogen.

There is an important relationship between malignant melanoma and nevocytic nevi (common pigmented moles). Ackerman found remnants of nevus cells within the dermis in 35 to 50 percent of all malignant melanomas that arise on the trunk and extremities (Roses et al. 1983). Thus,

(a)


281 LESIONS
276 MEN
POSTERIOR 166
ANTERIOR 115

(b)

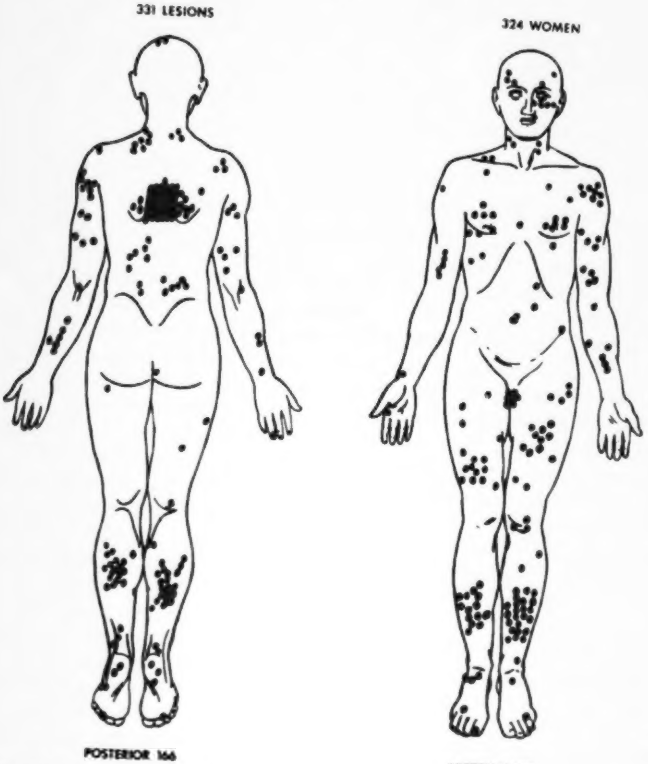

331 LESIONS
324 WOMEN
POSTERIOR 166
ANTERIOR 165

FIGURE 10-8 Distribution of superficial spreading malignant melanoma of the skin in (a) men and (b) women. SOURCE: New York University Melanoma Cooperative Group.

TABLE 10-1 Comparison of Anatomical Distribution of Nonmelanoma and Melanoma Cancers of the Skin

Site	Nonmelanoma (%)		Melanoma (%)	
	Men	Women	Men	Women
Head and neck	80	81	27	17
Upper limb	11	9	22	26
Trunk	7	6	38	22
Lower limb	2	4	13	35

SOURCE: Scotto and Fraumeni (1982).

nevocytic nevi are often present at sites where malignant melanomas occur. Of great importance is the fact that, more recently, certain types of nevocytic nevi have been identified clinically and histologically as "dysplastic" nevi (Elder et al. 1981). These are considered to be "precursor" lesions that portend an increased risk for malignant melanoma. They occur both sporadically and in families in which multiple members have numerous nevi that are histologically "dysplastic" (Lynch et al. 1983). "Dysplastic" nevi may be one of several types of aberrant proliferations of melanocytes that are associated with a broad spectrum of histologic and biochemical changes that range from hyperplasia of relatively normal-appearing melanocytes, through development of "dysplastic" melanocytes, and, finally, to the emergence of cancerous melanocytes, i.e., malignant melanoma (Holman 1983, Sagebiel 1983). The fact that "dysplastic" nevi occur with much less frequency on doubly clothed areas (buttocks in both men and women and breasts in women) is consistent with the concept that these precursor lesions are induced by exposure to sunlight. A few preliminary observations concerning the effect of UV radiation and other carcinogens on cells from patients who have dysplastic nevi suggest that there may be some aberrant responses of these cells to these DNA-damaging agents (Ramsay et al. 1982). Recent publications have suggested that as many as one-fifth to one-third of malignant melanomas in man have histologic contiguity with "dysplastic" nevi (Elder et al. 1981, Rhodes et al. 1983a). Should these preliminary data be confirmed, a major effort is mandated to identify these precursor lesions before they give rise to malignant melanomas. Also, in the context of this report, the role of UV-B in the induction of such "dysplastic" nevi is a most important area of needed research.

Nevocytic nevi of the nondysplastic type also occur more frequently on sun-exposed than on sun-protected areas (Kopf et al. 1978). For example, the lateral (outside) aspects of the arms have more nevocytic nevi than the medial (inside) aspects have . Doubly clothed areas such as the breasts of women and the buttocks of both men and women have fewer nevocytic nevi than have more sun-exposed sites. For persons of a given skin type, the number of nevocytic nevi on exposed areas increases with total cumulative exposure to sunlight during childhood and adolescence (Holman 1983). Sun-induced nevocytic nevi may be precursors of malignant melanoma. Holman (1983) demonstrated that the risk of superficial spreading malignant melanomas in western Australia was higher in persons with more nevi.

A recent report by Beral et al. (1982) concludes that an increased risk for developing malignant melanoma is associated with exposure to fluorescent light at work. Such lamps emit small quantities of UV-B as well as UV-A (Maxwell and Elwood 1983). Others have reported confirmatory (Pasternack et al. 1983) as well as discrepant (Rigel et al. 1983) results concerning the observation of Beral and coworkers. Much more work is needed in this newly identified controversy.

EVIDENCE AGAINST THE ROLE OF SUNLIGHT

Exposure to Sunlight

Although latitude gradients in the incidence of malignant melanoma are seen in the United States, Norway, Sweden, and Great Britain, much less striking, or even reverse gradients, are seen in western Australia, New Zealand, and central Europe. A partial gradient is noted in eastern Australia, where in Queensland the incidence is actually less in the tropics and in the subtropics (Lee 1982, Green and Siskind 1983, Urbach 1983). The expected trend of increased incidence with decreasing latitude is not seen in Finland when adjustments are made for place of residence (urban versus rural) (Teppo et al. 1978). The latitude gradient can also be confounded by skin types, genetic types, and occupation, such as in white collar versus blue collar workers (Beral and Robinson 1981).

In contrast to nonmelanoma cancers of the skin, which occur with much greater frequency in outdoor blue collar workers, malignant melanoma affects mainly the white collar, educated urbanite (Lee 1975, Holman et al. 1980a,b, Lee and Strickland 1980). Most cancers of the skin in humans that are induced by ultraviolet radiation occur in the later decades of life. In contrast, malignant melanoma tends to occur with highest frequency in the middle decades of life (Young et al. 1981).

In Hawaii, an area of high insolation, malignant melanoma in Caucasians occurs more frequently in immigrants than in the native (Hinds and Kolonel 1980). Presumably native Hawaiian Caucasians should be exposed to considerably more sunlight than should immigrant Caucasians. In Norway no significant difference was found between melanoma patients and controls as regards hair and eye color, time spent outdoors during leisure, and degree of solar exposure (Klepp and Magnus 1979).

Malignant melanomas arising in young children who have giant congenital nevocytic nevi are unrelated to sunlight exposure (Rhodes et al. 1982). Histologically there is relatively little solar elastosis in the skin in the vicinity of malignant melanomas in comparison with that frequently seen near basal cell carcinomas or squamous cell carcinomas (Brodkin et al. 1969, Larsen and Grude 1979).

Anatomical Distribution

The anatomical distribution of malignant melanomas in humans does not closely match the areas of highest accumulated UV-radiation exposure to the skin (Figure 10-8). About 75 percent of malignant melanomas occur on relatively unexposed anatomical sites (Crombie 1981). The match between the anatomical areas of highest exposure to the sun and areas of highest tumor concentration is much more convincing for basal cell and squamous cell carcinomas of the skin than it is for malignant melanomas. Some explain the high prevalence of malignant melanoma on the legs of women by the fact that they wear dresses, thus exposing this part of their anatomy more to sun. Others disagree, surmising that the amount of sunlight that is absorbed by the legs while standing erect is relatively small (Urbach 1983). Clearly, malignant melanoma can occur, albeit rarely, in areas that never are exposed to sunlight (e.g., anogenital areas). A recent report indicates that nonmelanoma cancers of the skin are seen more frequently in patients who have multiple primary malignant melanomas than in those who have a single primary malignant melanoma (Scheibner et al. 1981).

Genetic Origins

Some fraction of malignant melanomas, ranging from 1 percent (Duggleby et al. 1981) to 6 to 11 percent (Urbach 1983), appears to be of genetic origin.

Thus, evidence exists that some malignant melanomas are clearly not associated with exposure to sunlight; therefore, any perturbation of stratospheric ozone would not affect the incidence of such lesions. This evidence, however, does not rule out the participation of solar radiation in other types of malignant melanoma.

Although direct effects of sunlight on melanocytes may play a role in the development of malignant melanoma, sunlight exposure may also influence melanoma risk indirectly by affecting host factors that contribute to the outgrowth of transformed cells. For example, UV radiation abets the growth of nonmelanoma cancers of the skin in mice by altering the host immune response directed against those cancers (Kripke 1981). It is possible that such an indirect effect of UV radiation contributes to the induction of malignant melanoma as well. In fact, studies using a transplantable malignant melanoma of mice have shown that exposure of animals to UV radiation can potentiate the growth of a transplantable malignant melanoma that originally arose spontaneously (Kripke et al. 1979).

MALIGNANT MELANOMA IN ANIMALS

One obstacle to defining the contribution of ultraviolet radiation to the induction of malignant melanoma has been the lack of an appropriate animal model for this neoplasm. That is, malignant melanoma has not been induced in reproducible laboratory experiments by exposing any species of animal to light alone, including to UV-B by itself. Until recently, detailed experimental studies on the development of primary malignant melanomas have been limited to analysis of the genetic factors determining its occurrence. Two models have been used: the swordtail/platyfish system, in which a tumor-producing gene and its regulatory genes have been identified (Vielkind 1976, Anders 1983) and the Sinclair miniswine system, in which the development of melanoma also is determined genetically (Millikan et al. 1973, 1974; Manning et al. 1974; Hook et al. 1979). However, neither system is particularly well suited for studying the possible contributions of UV radiation to malignant melanoma induction.

Since 1949, reports on the induction of malignant melanomas and melanocytic lesions with chemical carcinogens in laboratory rodents have appeared sporadically in the cancer literature (Shubik et al. 1956, Ghandially and Barker 1960, Edgcomb and Mitchelich 1963, Rappaport et al. 1963, Klaus and Winkelman 1965, Vesselinovitch et al. 1970, Berenblum 1976, Clark et al. 1976). Most of these involved the induction of melanomas by topical application of the polycyclic hydrocarbon carcinogen, dimethylbenzanthracene (DMBA), although neonatal exposure of hamsters to urethan also was reported to be effective (Vesselinovitch et al. 1970). None of these models has been extended to include an analysis of the possible contribution of UV radiation as a cocarcinogenic agent, perhaps because of the low frequency of occurrence of malignant cancers in these animals.

There are two reported instances of the occurrence of malignant melanoma in mice exposed to UV-B radiation in conjunction with a second agent. Epstein et al. (1967) reported the induction of a small number of malignant melanomas in pigmented hairless mice treated with a single dose of DMBA to produce benign nevi, followed by chronic irradiation with UV-B. Kripke et al. (1979) described a single melanoma that arose in a haired, inbred C3H mouse treated with UV-B radiation, followed by chronic painting with croton oil. It is not possible to determine from these isolated reports whether the UV radiation was an essential or even a contributing factor to the induction of the melanomas. However, the occurrence of these malignant melanomas suggests that a rodent model might be developed for analyzing the contribution of UV-B radiation to their induction.

Two animal models for inducing malignant melanomas by chemical carcinogens have been identified recently. Pawlowski et al. (1976) reported that treatment of young albino guinea pigs twice weekly with DMBA resulted in the induction of metastasizing melanomas in 40 percent of 65 animals by 18 months. Berkelhammer et al. (1982) reported the induction of malignant melanomas in 2 of 20 inbred C57BL/6 mice, treated as neonates with a single dose of DMBA, followed by twice-weekly applications of croton oil. Thus, it currently should be feasible to use these systems to explore the possible role of UV radiation as a potentiating factor in the induction of these malignant melanomas.

A second possible role for UV radiation in the development of malignant melanoma is one in which the radiation affects the growth, rather than the induction of these neoplasms. Recent studies on the immunological effects of UV irradiation (Chapter 8) demonstrate that the rejection of certain tumors is impaired by repeated exposure of mice to UV-B radiation. This impairment is systemic and is not restricted to the site of irradiation. Although UV-radiation-induced fibrosarcomas and squamous cell carcinomas of the skin are the main cancers whose growth is accelerated in UV-irradiated hosts (Kripke 1981), two melanomas have also been found to exhibit this behavior. The B16 melanoma, which arose spontaneously in a C57BL/6 mouse in 1953, grows more readily in UV-irradiated than in unirradiated syngeneic hosts (Kripke 1977, Kripke et al. 1979, Bowen and Brody 1983). This is also the case with the K1735 melanoma (Kripke 1979) that was produced in a C3H mouse with UV-B radiation plus croton oil (Kripke and Fidler, unpublished data). In these instances UV radiation produces a systemic alteration that is conducive to tumor growth. This systemic alteration could be immunological, like the one responsible for enhanced growth of UV-induced skin cancers; alternatively, it could represent a biochemical change in which skin photoproducts have nutritive or growth-stimulatory effects on the proliferating tumor cells.

Such an indirect role for UV radiation in the pathogenesis of malignant melanoma is an attractive hypothesis to consider in assessing its role in human melanomas. In fact, on the basis of epidemiological data, Lee and Merrill (1970) postulated the existence of a "solar circulating factor." This factor, which is assumed to result from sunlight exposure, was evoked to explain the occurrence of melanomas on parts of the body that are not regularly exposed to direct sunlight. Studies with the transplantable malignant melanomas in mice exposed to UV radiation may offer some new insights into this possibility.

Finally, UV radiation has been shown to increase the capacity for metastases of cells irradiated in vitro (Fisher and Cifone 1981).

IMPLICATIONS

Because of the lack of laboratory models with which to study the effect of UV radiation on the induction of malignant melanomas, the precise mechanisms by which sunlight might cause or contribute to malignant melanoma is unknown. It is not even known which wavelengths in sunlight, if any, might be implicated. However, based on the considerations discussed earlier, it is probable that sunlight is a factor that contributes to the induction of certain human malignant melanomas. Nonetheless, current data do not permit us to conclude that sun exposure is the only risk factor for all malignant melanomas. Other possible factors such as hormonal influences (Holly et al. 1983), genetic factors, oncogenic viruses (Parson et al. 1974, Balda et al. 1975), and chemical carcinogens must be taken into consideration in the pathogenesis of malignant melanoma in humans (Lee 1982, Holly et al. 1983). Furthermore, current data do not permit us to project increases in incidence of and mortality from malignant melanoma due to decreases in stratospheric ozone.

The biochemical events that lead to the malignant proliferation of melanocytes are unknown. Furthermore, the precise role, if any, of UV-B in the malignant transformation of melanocytes is totally obscure at this time, although the systemic effects of UV radiation on the immune system strongly suggest important avenues for research (Morison et al. 1979, Hersey et al. 1983b).

On balance, the evidence presented in this section favors the hypothesis that sunlight is at least partially responsible for the induction of some malignant melanomas in humans. The precise wavelengths of electromagnetic radiation in sunlight that might cause the malignant proliferation of melanocytes are not known. Thus, an increase in UV-B radiation at the Earth's surface resulting from a decrease in stratospheric ozone will have important consequences for malignant melanoma only if the wavelengths of sunlight involved in photocarcinogenesis are in the UV-B range.

Clearly, if the amount of UV-B is increased by a reduction in stratospheric ozone, it is highly probable that this will result in an increase in nonmelanoma cancers of the skin. The data to implicate sunlight as a major factor in the pathogenesis of malignant melanoma in humans are much less convincing. Into the formula that will eventually be created and that will allow much more precise prediction of the incidence and mortality rates of malignant melanoma should be added a number of factors both unrelated and related to sun exposure that may decrease as well as increase malignant melanomas. Thus, chemical carcinogens and oncogenic viruses in the environment, more widespread use of effective sunscreens, changing life-styles and clothing styles, and influence of migration of Caucasians to geographic areas of high or low insolation are among the many factors that will have to be taken into account in the ultimate predictions of the incidence and mortality rates of malignant melanoma.

In conclusion, we have only circumstantial evidence that UV radiation (or UV-B) is related to malignant melanoma. It is clear that if there is a relationship between exposure to sunlight and incidence of malignant melanoma, the relationship differs from that observed for nonmelanoma cancers of the skin. An increase in UV radiation could, however, result in a relatively large number of persons who get intermittent, high-intensity sun exposure (MacKie and Aitchison 1982). Especially in those who tan poorly or have "dysplastic" nevi, this increased amount of UV radiation may exceed the carcinogenic threshold on melanocytes or induce immunosuppression that would result in a larger increase in the incidence of malignant melanomas.

RESEARCH RECOMMENDATIONS

To determine the effect of an increase of UV-B radiation on the incidence and mortality rates of malignant melanomas in humans, the following principal areas of research are recommended.

- Animal models should be developed to investigate the role of UV-B radiation in the induction and growth of malignant melanoma.
- The recently developed technology of culturing normal human melanocytes should be employed to study the effects of UV-B on the process of neoplastic transformation in vitro.
- Monoclonal antibodies directed against malignant melanoma antigens should be used to identify subclasses of malignant melanomas resulting from various etiologies.
- Additional epidemiologic studies are needed to identify further the risk factors for malignant melanoma and to create models that could be used to predict the

effect of increased UV-B radiation on the incidence and mortality rates of malignant melanoma.

- The role of precursor lesions of malignant melanoma should be determined in both experimental animals and humans with special emphasis on so-called dysplastic nevi.

11

Animal Studies of Photocarcinogenesis

Information from studies on experimental photocarcinogenesis in animals has been accumulated for nearly a half century (Blum 1959, Urbach et al. 1979). The NRC (1982) report and its predecessors dealt with the available biological data and made recommendations on acquiring needed information. In this chapter we present some background and a summary of relevent findings from laboratory studies reported since the 1982 monograph.

DOSE-RESPONSE RELATIONSHIPS

Several reports of studies on laboratory animals have discussed the relationship between stimulus (increased amount of a specified UV-radiation quality) and response (defined tumor endpoint). For example, Forbes et al. (1981) found that in albino hairless (Skh:HR) mice the median latent period for the production of skin tumors (median time to reach 50 percent incidence) is inversely proportional to the size of the daily UV-radiation dose. Additional experiments by De Gruijl and Van Der Leun (1980) extend the range of doses in this type of experiment. These authors conclude that the dose-response relationship can be represented by a cumulative log normal distribution. Their descriptive model of response time is the sum of two time intervals, one being dependent and the other independent of daily UV dose. They relate these intervals to tumor initiation and growth, respectively. According to De Gruijl and Van Der Leun, the time interval to accomplish tumor initiation is dose-related, but the interval for tumor growth is independent of the intensity of continued exposure. This would mean that once the neoplastic changes were put into action, the time required for development of tumors to a recognizable size would not be influenced by the amount of UV radiation in subsequent exposures.

Rundel has analyzed yet another set of laboratory animal data (1983a) as well as epidemiological data on human skin cancer (1983b). He presents the interpretation that UV radiation has a brief effect on tumor initiation and then becomes an effective dose-related promotor of tumor growth. This interpretation means that the probability of the growth of a tumor to a recognizable size (and thus to biological significance) is related to the amount of UV radiation received during tumor growth. By analogy others have demonstrated a change in relation of tumor response to initiating-UV-radiation dose, dependent on chemical promotion (Fry and Ley 1984). The contrasting interpretations of De Gruijl and Van Der Leun (1980) and Rundel (1983a, b) have quite different implications for assessing the consequences of changes in stratospheric ozone; at this time the preponderance of evidence would suggest that UV radiation enhances the growth of tumors.

A factor that is widely recognized, but seldom stated explicitly, is uncertainty about appropriateness and relevance of available laboratory models. Based on expediencies of experimental design, animal data tend to be drawn from studies measuring influences on tumor latent period, and on numbers of tumors produced, whereas clinical concerns tend to center on proportions of populations ultimately affected. It is for future studies to determine whether the laboratory and clinical observations relate to different parts of the same dose-response relationship.

TIME-DOSE RECIPROCITY

The development of erythema (sunburn) in human skin is an example of a photobiological response that is a direct function of dose, unaffected by the length of time required to deliver the dose (at least up to several hours). Parrish (1983) has reported a constant response per unit dose over UV-radiation delivery times ranging from nanoseconds to hours (approximately 12 orders of magnitude). Time-dose reciprocity in the carcinogenic response is evident over a much narrower range according to a number of studies described below.

One of the assumptions inherent in some of the predictions of human response to sunlight involves the concept of lifetime dose. The assumption is that the probability of developing skin cancer is directly related to accumulated lifetime dose of UV radiation, with the recognition, of course, that the contributions to the lifetime dose are made under various circumstances (e.g., for different sunlight intensities, durations of exposure, and environmental factors). However, the inherent variables can be too numerous for interpretation of the lifetime dose. Some of these variables have been tested in mice.

In repeated-exposure, long-term studies, the complexity of defining time, dose, and intensity is greater than is usually appreciated. In typical long-term carcinogenesis studies, time is implicit in the response parameter, whether it is measured as cumulative lifetime events, as prevalence at an arbitrary endpoint, or as average time to response. Such studies often involve chronic treatment with the test material, and the dose that produces an observed effect is obviously related to the time over which it was administered. When the number of deaths and responses is small at the (arbitrary) time-of-response measurement, the integral dose (amount per application times the number of applications) can be useful. However, when most animals respond, or if the measure of response is a time variable (average time to tumor development), the dose integral is partially defined by the response and acquires undesirable statistical properties. The usual solution to this problem is to express the dose axis in terms of delivery rate, e.g., amount per day. This, however, is a measure of intensity rather than of dose, and the resulting relationship is that of response to intensity with the proviso that treatment is chronic.

Although skin tumors have appeared in animals after single exposures to UV radiation, most studies on photocarcinogenesis involve repeated exposures over extended time periods. In studies where dose delivery has been a measured variable, the data indicate an increased carcinogenic effectiveness per unit dose for conditions involving attenuation of the dose (i.e., lower intensity or fractionation). For example, a specified total dose per week is more effective when given either in three or five fractions, than when given on one day (Forbes et al. 1981). The conclusion is supported by several other studies (Forbes 1982).

Over a narrow range of time intervals (45 min to 2 h), delivery of specific integral doses can be achieved by varying either the duration or intensity of irradiation, without altering the carcinogenic effectiveness of the dose (Forbes et al. 1982a).

Taken together, the contemporary lines of experimental data suggest that (1) over a fairly narrow range of dose-delivery schedules, effectiveness is proportional to dose, whether dose is varied by intensity or duration; (2) over a wider range of dosing schedules, effectiveness becomes inversely proportional to intensity and directly proportional to periodic dose duration; and (3) too little information is currently available to permit translating conclusions (1) and (2) into an equation that will accurately predict response to more than a few of the possible UV-radiation exposure conditions.

ACTION SPECTRA

Blum's classic work (1959) showed that the portion of the UV spectrum associated with human erythema is effective in producing skin cancer in animals. Using narrower bands of radiation, Freeman (1975) suggested that the action spectrum for photocarcinogenesis in mice parallels the human erythema action spectrum at least at the wavelengths tested. The vascular responses of various mammalian species exposed to UV radiation exhibit qualitative differences, and so it is important to make as many comparisons within one species as possible.

A recent development was the demonstration (Forbes et al. 1982a, Cole et al. 1983) that the action spectrum for minimal erythema in humans corresponds closely to acute response action spectra in hairless mice (principally for the edema response) (Figure 11-1). These monochromatically derived weighting functions accurately predict the effectiveness of polychromatic sources for producing the same response (over the fairly limited series of spectral qualities tested). The weighting functions also reasonably predicted the effectiveness of a series of polychromatic spectra for producing carcinogenesis in hairless mice. Thus, in the mouse, the rather long extrapolation from a monochromatic, acute-effects action spectrum to a polychromatic, chronic-effect action spectrum has been partially verified, lending greater credibility to the use of this extrapolation in humans. Moreover, the demonstration of qualitatively and quantitatively similar acute response spectra between the two species strengthens the extrapolation of carcinogenesis studies in mice to those in humans.

This is one method of identifying an action spectrum, namely, by selecting weighting functions and testing

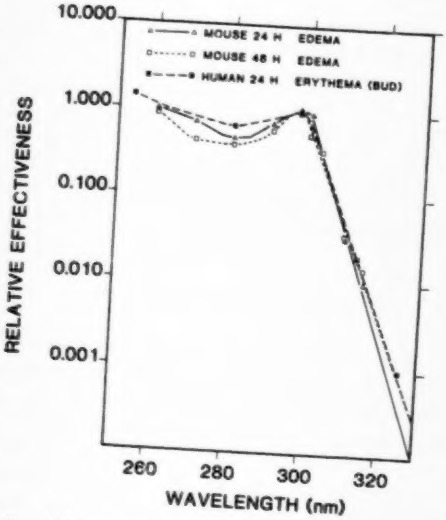


FIGURE 11-1 Semilogarithmic plot comparing the mouse edema action spectra (observed at 24 h and 48 h postirradiation) with the BUD action spectrum for minimal perceptible erythema in humans observed at 24 h. The spectra have been normalized at 297 nm. SOURCE: Reprinted, with permission, from Cole et al. (1983), Photochemistry and Photobiology, Vol. 37, © 1983 Pergamon Press, Ltd.

their ability to describe response data. Rundel (1983a) had developed another approach in which a weighting function is derived directly from the data. Differences in polychromatic source spectra are treated as if they were discrete wavebands, and the contribution of each waveband to the total effectiveness is calculated. With this method, given enough data, an action spectrum can be described completely from the biological response. One distinct advantage of this approach is that it bypasses the technical and interpretive problems inherent in monochromatic sources, including questions of waveband additivity. Rundel (1983a) has used the data reported by Forbes et al. (1982a) to develop an action spectrum for carcinogenesis in hairless mice. This weighting function is similar to one describing damage to DNA.

Both approaches suffer from the small number of spectra available for analysis and from the lack of information at wavelengths much less than 300 nm, where spectral changes related to stratospheric ozone modification would be most pronounced (see Chapter 12). Consequently, until additional studies are commissioned, the projections can be made only by extrapolating the weighting functions beyond the areas supported by existing data. In addition, both approaches make the simplifying assumption that the action spectrum remains constant throughout the dosing period. In fact, the relative effectiveness of parts of the spectrum could change with age or with the effects (e.g., hyperplasia) of initial UV-radiation exposures (De Gruijl and Van Der Leun 1982b).

Effectiveness of UV-A

"Blacklight" (BL) fluorescent lamps are a convenient source of UV-A. Although skin tumors have been produced in animals exposed to BL lamps (Zigman et al. 1976), the inducing agent was not positively identified. These lamps do have a measurable output in the UV-B range of the spectrum (Forbes et al. 1976). When these lamps are filtered with window glass, animals can be exposed 8 h/day for several months and remain virtually free of neoplasia; however, when the same daily dose is delivered at reduced intensity over a 24-h period and the animals are exposed continuously for 10 weeks, the skin of hairless mice exhibits acute and chronic changes (Forbes 1974) including the development of carcinomas (Forbes et al. 1982b). Similarly, Van Weelden et al. (1983) have reported production of tumors, using 12-h/day exposure to UV-A alone. Thus, although UV-A radiation is considered an inefficient producer of biological damage, under some circumstances it will produce many of the changes associated with exposure to UV-B radiation. We do not know whether the same biological target is affected by the entire UV spectrum, whether damage is repaired similarly, nor whether the effects are entirely mediated by changes within the skin. There is some reason to believe that indirect effects are very significant with some types of responses.

WAVELENGTH INTERACTIONS

It is possible that various parts of the spectrum may act in other than an additive fashion. With erythema as an endpoint, for example, evidence has been presented to indicate that the wavelengths longer than 320 nm either enhance or inhibit the effectiveness of UV-B radiation:

Van Weelden (1980) reported that effectiveness of an exposure to UV-B radiation can be decreased by subsequently re-exposing the area to UV-A and visible radiation; in contrast, Willis et al. (1977) reported that exposure to UV-A radiation enhances the effectiveness of UV-B radiation, particularly when the exposure to UV-A radiation precedes the exposure to UV-B radiation. Ying et al. (1974) have reported that the effect is no greater than what can be attributed to additivity of effectiveness by various portions of the spectrum. Willis et al. (1981) also reported that the response to repeated UV-A and UV-B-radiation exposures (epidermal hyperplasia and solar keratosis) has an interactive effect greater than an additive one. Recent data from a carcinogenesis study by Willis and Menter (1983) using simulated solar UV radiation are difficult to interpret, and the authors postulate a complex interaction by the wavelengths involved.

Van Weelden et al. (1983) have reported that preexposure to UV-A can enhance slightly the carcinogenic effectiveness of daily UV-B (FS sunlamp) exposures. Whether this design simulates preexposure to morning sunlight (which is relatively poorer in UV-B) is not known.

Currently there appears to be little evidence that wavelengths greater than 320 nm produce interactive effects in mammalian carcinogenesis comparable to their influence in other (cellular, microbiological, plant) systems.

RESEARCH RECOMMENDATIONS

- Dose-response data for UV-B-induced tumors are needed both below and above the currently available range in order to distinguish between alternative mathematical models.
- More data are needed relating both the total dose and the delivery rate to tumor induction and development.
- Biological action spectra need to be extended to the critical region in the range of 295 to 300 nm.
- Data are needed for effects produced by UV-B in the presence of several different levels and temporal sequences of UV-A to explore the possibility of interactions among effects at different wavelengths.

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Molecular and Cellular Studies

NRC (1982) contained an extensive review of the results of studies of the effects of UV radiation upon biomolecules and cells. The ability of molecular and cellular studies to provide a solid scientific foundation for connecting photomolecular events with consequential photobiological responses in higher organisms was delineated. We would suggest that, in fact, rapid progress in understanding the responses of higher organisms to UV radiation occurred only after the elucidation of some of the molecular and cellular alterations caused by UV radiation. Certainly any estimation of the possible biological consequences of increased UV-B radiation in terrestrial sunlight would benefit from knowledge derived from molecular and cellular studies.

Key findings discussed in NRC (1982) are summarized briefly as follows: absorption of light by DNA in the range of wavelengths between 240 and 320 nm leads to modifications of various kinds in its chemical structure and can cause killing, mutation, or transformation of a large variety of bacterial and mammalian cells. While more than a dozen types of photoproducts have been detected in DNA exposed to UV radiation, the biochemical and biological sequelae of only one class, the so-called pyrimidine dimers, have been elucidated in some detail. Primarily because of the employment of enzymes that function to repair or reverse pyrimidine dimer damage in DNA, it has been possible to demonstrate that these lesions can be responsible for killing, mutation, and transformation. Pyrimidine dimers and their repair have been observed in human skin exposed to UV radiation. The extremely high prevalance of skin cancer in the sun-exposed areas of patients with the disease xeroderma pigmentosum has been associated with defects in one or more mechanisms for repair of DNA photoproducts in their cells.

MECHANISMS OF UV-B-INDUCED DAMAGE

A reduction in stratospheric ozone is predicted to have maximum impact in the terrestrial solar spectrum in the UV-B region (from 280 nm to 320 nm). While a great deal is known about the effects of light of shorter wavelengths, relatively little is known about the effects of UV-B on DNA in cells. There are many indications that the damage caused by radiation in this wavelength region occurs by different mechanisms from damage caused by radiation of longer or shorter wavelengths. There is general agreement that in bacteria the initial steps in UV-mediated damage by wavelengths above 320 nm are different from those at wavelengths below 300 nm. Above 320 nm, pathways involving oxygen-mediated damage appear to be dominant (Peters and Jagger 1981), although some formation of cyclobutane pyrimidine dimers is also observed (Webb and Brown 1982). The oxygen-mediated damage occurs through creation of activated oxygen species by the interaction of molecular oxygen with photoexcited biological chromophores, which, by and large, have not yet been identified. Below 300 nm, damage occurs predominantly through direct absorption of UV radiation by DNA and subsequent DNA photochemistry. But the boundaries between the two types of effects are ill-defined and fall into the wavelength region that is strongly affected by ozone changes.

In the region from 240 to 320 nm, the action spectrum for a variety of responses in bacterial and mammalian cells associated with DNA matches the DNA absorption spectrum quite well, except at the longer wavelengths. The latter are less efficient than expected from absorption alone (NRC 1982). It is not clear whether this effect occurs because these wavelengths are less efficient at causing particular types of damage or because the damage caused by these wavelengths is more easily repaired.

Recently, comparative studies of different wavelengths have been extended to human cells in culture. It was found that a xeroderma pigmentosum (XP) cell line shows a normal response to wavelengths longer than 313 nm. Thus, the repair of DNA damaged by these wavelengths does not require the DNA repair enzyme system(s) that is deficient in cells from XP patients (Keyse et al. 1983). Alternatively damage caused by these wavelengths may simply be irreparable.

More needs to be known about the molecular mechanisms responsible for lethal and mutagenic DNA damage before the effects of different wavelengths can be understood fully. If absorption of radiation directly by the DNA is an important determinant, UV-B would be predicted to cause enhanced damage in regions rich in guanine-cytosine. The absorption spectrum of guanine (G) and cytosine (C) is shifted to the red significantly compared with that of adenine (A) and thymine (T). Most of the excitation generated by photoabsorption remains localized reasonably near the absorbing chromophore. For example, as longer wavelengths are used, the relative yield observed for photodimers containing cytosine increases compared with dimers containing thymine (Childs et al. 1983). The DNA of higher organisms has roughly equivalent contents of AT and GC pairs. However, in several cases, nontranscribed spacers have been shown to be rich in AT, while coding regions were rich in GC. Hence, damage at the long-wavelength absorption edge of DNA would occur preferentially in the coding regions in some genes. In view of the fragmentary nature of the available data, however, it is premature to conclude that such effects would be sufficiently general to have broad biological significance.

If singlet-triplet absorption or photosensitization are important damage mechanisms, the effect of wavelength on the distribution of photoproducts at particular sites could be very different from that seen in direct singlet absorption. For example, triplet excitation in general can migrate, and in normal, right-handed double-helical DNA it locates on thymine bases. The migration rates will be very sensitive to local variations in DNA structure. Hence, the spectrum of damage might be expected to be sensitive to structural variations.

It is clear that currently we are highly uncertain about which factors are most important. However, recent advances in the ability to manipulate specific DNA sequences now make it feasible to answer some of the pertinent questions. It is possible to irradiate purified DNA sequences with any combination of monochromatic wavelengths desired, and then to detect the specific residues that have been photodamaged, using modern ladder sequencing techniques. Application of these techniques should allow a systematic exploration of the effects of UV-radiation on DNA.

Z-DNA PHOTOCHEMISTRY

It has recently become clear that sections of DNA in eukaryotic cells may adopt a left-handed helical structure (Z-DNA) rather than the normal, right-handed helical structure. The evidence for this is principally the observation that antibodies specific for Z-DNA react with a variety of chromosome and nuclear preparations (Jovin et al. 1982, Leng et al. 1982, Pardue et al. 1982). There is also some evidence that this unusual DNA structure may be prominent in control regions of mammalian genes. For example, sequences capable of switching to the Z form are present in the enhancer sequences near the replication origin of the tumor virus SV40 (Nordheim and Rich 1983). Enhancer sequences are powerful transcriptional activators that may play critical roles in tissue-specific and developmentally regulated gene expression. Enhancers activate genes located on the same DNA molecule, but the enhancer may be some distance from the gene itself. The currently accepted model is that enhancers are RNA polymerase entry sites: the polymerase binds to DNA at the enhancer and then searches for nearby promoters, which are a second level of regulation that will determine whether the gene will ultimately be transcribed to produce a messenger RNA.

Z-DNA has approximately four times the absorption cross section at 295 nm that B-DNA has (van de Sande and Jovin 1982). The 260-nm absorption peak of DNA shifts to longer wavelength upon conversion to the Z form in poly d(G-C) and poly d(A-C) • d(G-T) (McIntosh et al. 1983). Thus it is conceivable that Z-DNA could be an important target for radiation in the wavelength range most affected by ozone reduction. Virtually nothing is known about the photochemistry of Z-DNA except for a recent report suggesting that it is surprisingly less susceptible to singlet oxygen-mediated photodamage (Feldberg et al. 1983).

CHEMICAL STRUCTURE OF DNA PHOTOPRODUCTS

Despite decades of work on the products of DNA produced by UV radiation, we still have an incomplete understanding of which products are really important for lethal, mutagenic, and other biological effects. Particular DNA sequences are hotspots for UV mutagenesis, and this may be related not just to the actual sequence but also to particular DNA secondary or tertiary structures (Foster et al. 1982, Todd and Glickman 1982). Systematic study is needed to explore whether specific sequences act at the level of initial photoexcitation, particular photochemical product, or repair pathway. As indicated earlier, techniques are now available that will greatly facilitate studies of the photochemistry and photobiology of particular DNA sequences.

Recently it has been suggested that certain products, such as pyrimidine 6:4 dimers, may be particularly mutagenic (Haseltine 1983). In these products a bond is formed between the 6 position of a 5' pyrimidine and the 4 position of the neighboring 3' pyrimidine after loss of the 4 exocyclic amino or keto group. The 6:4 dimers occur predominantly at T-C and C-C sequences. This reaction pattern matches the sequence bias seen for some mutational hotspots (Brash and Haseltine 1982). There is also new evidence that purine-pyrimidine products form in DNA after UV irradiation (Bose and Davies 1982). Such damage in a self-complementary sequence such as T-A could potentially occur on both strands, leading to an irreversible alteration in genetic information.

NONTARGETED MUTAGENESIS

A new level of complexity in the mechanism of radiation damage of DNA has been introduced by recent studies on the nature of nontargeted mutagenesis. New recombinant-DNA technology can be used to produce DNA molecules with particular types of damage localized at specific sites or regions and then to reintroduce these molecules into living bacterial cells. Clones of these cells amplify the result of repair of individual DNA molecules and thus allow events involving single molecules to be studied. Such techniques have been used to show that damage of DNA at a specific site may lead to mutants at other sites far removed from the site of damage (Livneh 1983). The general nature of this phenomenon, termed nontargeted mutagenesis, needs to be explored. The general notion is that certain types of damage stop DNA replication, threatening the survival of the organism. This type of damage leads to induction of a set of drastic repair functions, collectively termed the SOS repair system. One of the functions involved is an error-prone DNA polymerase. In *Escherichia coli* the induced enzyme may be an altered form of DNA polymerase I, which repairs DNA damage at the cost of introducing mutations at the damaged site and elsewhere (Lackey et al. 1982).

Other than for bacteria, little is known about either the damage required to induce the SOS repair systems or the full extent of the biological consequences once they are induced. At least some current data suggest that nontargeted mutagenesis is not a major factor in the overall rate of bacterial mutagenesis (Foster et al. 1982), but it may be quite important in yeast (Bridges 1983).

SENSITIVE ASSAYS FOR DNA DAMAGE

Once the genes that respond to the initial events after DNA damage are identified, it becomes possible to devise extremely efficient and sensitive tests to monitor damage. These tests can involve either fusions of genes that respond to damage to other genes that are more easy to assay directly or immunological detection of the products of the damage-responsive genes. The tests are well developed for bacteria, and could greatly simplify such tasks as obtaining rational biological action spectra.

In *E. coli* the *recA* gene plays a key role in the response of the cell to UV damage by controlling the production of a number of repair enzymes. Treatments that inhibit DNA synthesis or damage DNA cause a rapid rise in the synthesis of the *recA* protein. This phenomenon can be monitored conveniently by quantitative immunoassays (Karu and Belk 1982, Salles and Paoletti 1983) using specific antibodies against *recA* protein. Even more general are assays based on fusing the control region of the *recA* gene to the structural regions of genes with easily assayable products (Casaregola et al. 1982, Smith 1983, Smith et al. 1984).

Similar assays can be constructed to monitor DNA damage in higher cells. The first step in constructing such tests in higher organisms is to identify proteins in these organisms that are made in response to UV damage of cells. Yeast is currently the only eukaryote for which the genetics of response to UV damage is extensively characterized. Compared to *E. coli*, the repair of DNA damage in yeast appears to be incredibly complex, since more than 95 mutations affecting DNA repair have been identified, implying that a large number of different gene products are involved (Haynes and Kunz 1981). However, it is probably unfair to generalize this result to predict a similar complexity for mammals. Yeast has evolved to live on surfaces exposed to high light intensities. (It is remarkable that *E. coli* has any photorepair capability, considering its most frequent habitat). The situation in humans remains to be clarified. The gene fusion vector approach (Casadaban and Cohen 1979) is a powerful tool for the identification of genes that have altered expression in response to UV radiation. It has been used to identify many UV responsive genes in *E. coli* (Kenyon and Walker 1980, Elledge and Walker 1983), and a similar approach could well be applied to plants and animals to locate genes involved in repair. Note, however, that this approach failed to identify directly the critical *recA* protein in *E. coli*, and thus might also miss critical proteins in other organisms.

ROLE OF MEMBRANE PHOTOOXIDATION

Kochevar and Yoon (1983) have demonstrated that UV-B light can affect oxidation of lipid components of protein-containing biomembranes, apparently via the sensitizing effects of tryptophanyl residues. Earlier Mukai and Goldstein (1976) showed that malondialydehyde, a product of the oxidation of polyunsaturated fatty acid side chains, is able to cause mutations in the Ames salmonella test system. Generally, cells cannot sustain extensive membrane damage, and so membrane photooxidation is expected to produce toxic responses rather than surviving mutants.

RESEARCH RECOMMENDATIONS

A number of recommendations for research on some unclarified issues in the area of the effects of UV radiation on cells in culture were made in NRC (1982). Their aim was to provide important guidance for research on the effects of UV radiation on plants, animals, and humans. None of these recommendations has been carried to completion. In addition, current results suggest a number of additional research needs.

- More extensive studies in animal and bacterial cells on the action spectra for lethal and mutagenic events in the wavelength region from 280 to 320 nm are needed. Studies are also needed to identify any repair pathways or products of DNA damage that may be specifically favored or especially important in this wavelength range.
- Systematic studies of the photophysics, photochemistry, and photobiology of Z-DNA are needed. There are really two basic issues that should be explored in these studies. The first is the nature and susceptibility of Z-DNA to photodamage. The second is the nature and efficiency of processes that repair damaged Z-DNA.
- New recombinant-DNA techniques should be used to characterize the particular photoproducts and DNA sequences most sensitive to UV-B radiation.
- Nontargeted mutagenesis should be studied in both bacteria and higher plant and animal cells.
- Existing sensitive assays for DNA damage, using modern recombinant-DNA and immunological methods, should be applied to examine UV-B effects on bacteria. Genes in higher cells comparable to the *recA* gene of *E. coli* should be identified so that similar tests can be constructed in higher cells.
- The role of membrane photooxidation in the oxygen-dependent toxic effects of light in the wavelength range above 280 nm should be assessed. The oxygen dependence of mutational events in mammalian cells in culture induced by light needs to be studied.

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Effects of UV-B Radiation on Plants and Vegetation as Ecosystem Components

INTRODUCTION

While there has been a casual interest in the relationships between solar ultraviolet radiation and productivity of terrestrial plants for more than a century, it has only been within the last 20 years or so that much of a definitive and quantitative nature has been learned. The advances began in the 1950s and 1960s somewhat before the implications of possible stratospheric ozone depletion were appreciated. The movement into this field of botanical photobiology was aided in several ways. There was, of course, considerable improvement in biophysical techniques and instrumentation in those years right after World War II and with the initiation of the space age. Moreover, there was in those same years rapid development of understanding in the fields of plant physiology, photobiology, and plant physiological ecology.

We still know relatively little of the effects of solar and sky ultraviolet-B radiation on the growth and physiological processes in the seed plants that cover the Earth's continents and are the primary producers of food for all other organisms including mankind. We know even less about the implications of these effects on natural and crop ecosystems and the interactions within these systems. Since it was suspected, rather early, that UV irradiance was greater on high mountains in spite of its absorption by stratospheric ozone, there was considerable speculation about the effects of such irradiance on the growth and structure of alpine plants. However, alpine ecologists did not have the instrumentation or knowledge to investigate this under natural and simulated conditions until the work of Caldwell (1967, 1968). His results gave badly needed impetus to research on the UV-B relationships not only of high-mountain plants and their environments, but also of crop plants.

So much research on UV and plants has taken place since 1950 that there was great need for synthesis and reviews of what was known. Klein (1978) did a thorough job of this for the physiology of near-ultraviolet, while Caldwell (1981) was equally thorough in reviewing the ecological effects of solar ultraviolet irradiance on plants and their environments with special reference to ultraviolet-B. Both of these papers should be consulted for basic information on UV-plant problems. In addition, a workshop on the effects of ultraviolet radiation on plants was held in New Delhi, India, in November 1982; the workshop proceedings have now been published (see Björn and Bornman 1983).

NATURAL UV-B ENVIRONMENT AND ADAPTATIONS TO IT BY PLANTS

Gradients in Ultraviolet Irradiance

Based on the thicker stratospheric ozone layer in the polar regions, lower sun angles in such regions, and scattered measurements of UV-B irradiance at different latitudes, it was known that a latitudinal gradient of UV-B irradiance must exist at the surface of the Earth. An altitudinal gradient was also known. These data were generalized and somewhat qualitative until measured quantitatively from the equatorial mountains to the Arctic within the arctic-alpine life zone in the late 1970s (Caldwell et al. 1980). Along this latitudinal-altitudinal gradient, daily total visible irradiance at the solar radiation maximum varies only by a factor of 1.6 from Arctic to tropics. In contrast, maximum integrated biologically effective UV-B irradiance can vary by almost a full order of magnitude (a factor of 7) along the same gradient (Table 13-1). In addition to the natural latitudinal gradients in ozone thickness, solar angles, and elevation above sea level, this steep UV-B gradient is partly the result of an optical amplification effect that is due to a combination of selective atmospheric wavelength attenuation and the pronounced wavelength dependence of biological action spectra. The "biologically effective" radiation is based on the generalized plant damage action spectrum (Caldwell 1971), while the "DNA-effective" radiation is based on the DNA damage action spectrum of Setlow (1974).

TABLE 13-1 Integrated Effective Daily UV-B Radiation at Different Latitudes and Elevations During Seasonal Solar Radiation Maximum (in J/m^2)

North Latitude	Elevation (m)	Daily UV-B Dose		Calculated Daily UV-B Irradiation[a]		Calculated Daily UV-B Irradiation[b]	
		Biologically Effective[c]	DNA-Effective[d]	Biologically Effective[c]	DNA-Effective[d]	Location (Near Sea Level)	DNA-Effective[d]
0°	3,000-4,400	2,810	175	2,744	193	Balboa, Panama (9° N)	121
20°	3,000	2,597	145	2,563	168	—	—
40°	3,350	1,927	102	1,876	107	—	—
40°	1,500	1,462	72	1,618	93	Rockville, Maryland, USA (39° N)	42
70°	15	568	24	597	28	Barrow, Alaska, USA (71° N)	17

[a] From the theoretical model of Green et al. (1980).
[b] From average measurements of Klein and Goldberg (1978) during month of maximum solar radiation.
[c] Based on the action spectrum for generalized plant damage (Caldwell 1971).
[d] Based on the action spectrum for DNA damage (Setlow 1974).

SOURCE: Adapted from Caldwell et al. (1980).

Some Adaptations by Plants to Latitudinal UV Gradient

Field measurements of optical properties of leaf epidermis in relation to UV-B have been made with a number of kinds of plants along the latitudinal gradient (Robberecht et al. 1980). Mean epidermal transmittance of UV-B to the mesophyll of plant leaves in situ on equatorial and tropical high mountains was less than 2 percent. At higher latitudes, such transmittance exceeded 5 percent. Although the latitudinal solar UV-B gradient represents more than a seven-fold difference (Arctic to tropics) in daily integrated UV-B irradiance, the calculated mean effective UV-B irradiance at the top of the leaf mesophyll of tropical high-mountain species is not substantially different from that of leaves at higher latitudes. This is due mainly to absorption of UV-B in the epidermis of tropical plant leaves, probably by flavonoids and related phenolic compounds. Some light-colored glaucous or pubescent leaves also reflect UV-B, although such leaf surfaces, while reflecting visible light, do not necessarily reflect ultraviolet. Silver-sword (Argyroxiphium sandwicense) on the upper slopes of Haleakala in Hawaii had the highest UV-B reflectance of any plant measured (around 40 percent).

Many plants on tropical high mountains have vertical or steeply inclined leaves. This habit may aid in reducing the UV exposure, but since 40 to 70 percent of the solar UV-B flux in those places is in the form of scattered radiation from sky and clouds, such leaves still receive a sizable fraction of the global UV-B irradiance at the upper surface of the epidermis. Reflectance of UV-B from nearby snowbanks can also add considerably to the UV-radiation load of vertical foliage.

EFFECTS OF INCREASED UV-B IRRADIANCE ON PLANT GROWTH AND STRUCTURE

Since 1980 considerable evidence has accumulated that UV-B radiation is detrimental to the growth of crop plants. It is also known that there is an interaction between UV-B and photosynthetically active solar radiation expressed as photosynthetic photon flux density (PPFD). In full sunlight, the effects of UV-B on total dry-matter production in soybean was relatively unaffected, as compared with reduced production at light levels with lower PPFD (Teramura 1980). In contrast, maximum UV-B irradiance (70 milliwatts per square meter [mW/m^2]), which is that in full sunlight in June at Gainesville, Florida (29°36'N), resulted in a 35 percent reduction in growth of wheat. Teramura also found that both wheat and soybean are affected even by low irradiance of UV-B (17.5 mW/m^2) in regard to leaf numbers, total leaf area, dry-matter production, dry weights, and plant height. While wheat and soybean reacted slightly differently to UV-B, the effects of ultraviolet irradiance were of less magnitude at higher PPFDs.

Adverse effects of UV-B vary with genetic types within a species. For example, 19 genetic varieties of soybeans were grown in controlled-environment chambers under combinations of PPFD and five levels of UV-B irradiance (DNA weighted mW/m^2) (Biggs et al. 1981). Plants of all of these cultivars showed some stunting, leaf chlorosis, and loss of apical dominance under UV-B, but differed markedly in the genetically based effects of ultraviolet stress. Leaf area was reduced under increasing UV-B 43 to 78 percent depending on the cultivar, total dry weight was reduced 27 to 60 percent, and plant height was reduced 42 to 63 percent. Since these measurements were made in controlled-environment chambers, extrapolation to field conditions is difficult.

Crop plants of the family Cucurbitaceae (squash, pumpkin, cucumbers, melons, etc.) seem to be particularly sensitive to UV-B irradiance; the reasons are not known. Seeds of Cucurbita pepo (pumpkin) were allowed to germinate and grow in a Fiberglas greenhouse under two levels of UV-B irradiation and also under controlled conditions without UV-B (Sisson 1981). Absorbance of UV-B by extracted flavonoid pigments and other compounds increased with time and level of UV-B radiation impinging on leaf surfaces. This indicates that there can be acclimation or adjustment to UV-B within the life spans of some kinds of plants. In spite of this increase in absorbance of UV-B, it was insufficient to protect the photosynthetic apparatus or leaf growth processes completely. Leaf expansion was repressed by daily exposure to 1,365 joules per square meter per day (J/m^{2}d) (close to that in clear sunlight) of biologically effective UV-B but not by exposure to 660 J/m^{2}d.

Since germination and early seedling growth are very important in the establishment of a crop, some further attention has been paid to this. Tevini et al. (1983a) planted seeds of cucumber (Cucumis), bean (Phaseolus), and radish (Raphanus) under radiation at several levels of UV-B in a temperature-controlled growth chamber. The rate of germination decreased under the highest levels of UV irradiance to about 60 percent of that of seeds in the control. Hypocotyls were increasingly inhibited in growth under increased levels of UV-B. In cucumber, even the lowest level of UV-B radiation prevented elongation of hypocotyls. Fresh weight, dry weight, and leaf area were all smaller in plants exposed to UV-B. The greatest effect was on leaf area, and also on photosynthetic pigments (chlorophylls). Leaf surface structure, as examined with the scanning electron microscope, was progressively damaged with increasing dose rate of UV-B. In cucumber, stomatal number on both sides of the cotyledons was markedly lower under UV-B radiation. UV-B at enhanced levels of irradiation caused reduced seedling growth in all three species of these crop plants. As has been found in other experiments (Tevini et al. 1983b), cucumber was the most sensitive and was strongly affected even at moderate dose levels.

Recently, Teramura (1983) reviewed the current knowledge of the effects of UV-B on the growth and yield of crop plants. The following physiological characteristics are sensitive to UV-B radiation:

- Photosystems I and II
- carboxylating enzymes
- stomatal resistance
- chlorophyll concentration
- soluble leaf proteins
- lipid pools
- carbohydrate pools
- epidermal transmission

The sensitivity of these parameters apparently leads to the pronounced inhibition of growth observed at the level of the whole plant. Most of the effects have been shown, so far, only under controlled-growth-chamber conditions. The exception is epidermal transmission, which has been measured in the field (Robberecht et al. 1980). One of the problems with growth-chamber results is that UV-B effects are accentuated by the low levels of PPFD in most growth chambers. About 30 percent of crop species tested show some, but not complete, resistance to UV-B; about 20 percent are extremely sensitive.

EFFECTS OF UV-B IRRADIANCE ON WATER BALANCE AND PHOTOSYNTHESIS

There is, of course, a strong interaction between carbon dioxide uptake through leaf stomata and water loss by transpiration through the same apertures as they open and close. Ultraviolet-B radiation causes a decrease in stomatal resistance in the very sensitive crop plant, cucumber (Teramura et al. 1983a). This increases loss of water by transpiration and probably results in wilting and water stress, thus impairing photosynthesis. Also, Teramura et al. (1983b) recently have found that a combination of UV-B radiation and mild drought stress produces a greater reduction in photosynthesis during the early growth of soybean plants than is produced by either of these environmental stresses independently. When intregrated through time, this results in less productivity of the soybean plants. Older plants of soybean, however, are less sensitive to ultraviolet-B stress than they are to drought stress.

However, it is now known that the photosynthetic processes are even more directly affected by UV-B irradiance. For example, Sisson found in pumpkin (Cucurbita pepo), which is related to cucumber, that photosynthesis in seedlings was depressed by UV-B irradiance. This depression was especially evident during the ontogenetic period when normally photosynthetic activity reaches its maximum.

Inhibition of photosynthesis by UV-B is more pronounced in species and ecotypes from the higher latitudes of the Arctic than from ecotypes or closely related species from the high mountains of the middle latitudes in western North America or those from the high tropical mountains (Caldwell et al. 1982). The difference in photosynthetic inhibition caused by UV irradiation of arctic (Alaska) and alpine ecotypes (the latter from the Rocky Mountains of Colorado and the Sierra Nevada of California) of Oxyria digyna (L.) Hill could not be attributed solely to differences in UV flux penetrating to mesophyll tissues. Also, arctic ecotypes of this species exhibited short-term fluorescent transients indicating damage to the oxidizing side of Photosystem II, which is part of the photosynthetic light reaction where chlorophyll releases oxygen from water. There was no indication of this in the alpine ecotypes. Thus, there is a genetic difference within Oxyria in regard to the sensitivity of its photosynthetic systems to UV-radiation that is related to the position of the population on the latitudinal UV-B gradient. Iwanzik et al. (1983) also found that Photosystem II in spinach chloroplasts was inhibited by UV-B. However, their results suggest that the targets may be the Photosystem II reaction centers themselves.

There are two main photosynthetic pathways in the higher plants: they are denoted C_3 and C_4. The C_3 pathway is so designated because the first photosynthetic product derived from carbon dioxide is 3-phosphoglycerate, a sugar phosphate containing three carbon atoms in each molecule. In sugarcane, corn, and other C_4 plants, the first photosynthetic products, such as oxaloacetic acid, contain four carbon atoms in each molecule. The end products in each pathway are the same: sugars and starch. The principal enzyme in the C_3 mode is ribulose biphosphate carboxylase (RuBP carboxylase), while that in the C_4 pathway is phosphoenolpyruvate carboxylase (PEP carboxylase). Plants with the C_3 pathway grow from equatorial regions to the Arctic, but C_4 plants seem to be restricted to regions with warm summers, no matter how cold the winters. Among crop plants, soybeans, peas, and tomatoes (C_3) and corn (C_4) were grown in greenhouses at UV-B levels to be expected if stratospheric ozone were reduced by 6, 21, and 36 percent (Vu et al. 1982). Leaves of all three of the C_3 crop species were generally low in RuBP carboxylase activity when exposed to any UV-B level. This was statistically significant at all three UV levels for soybeans and peas; it was significant only at the two higher UV levels for tomato. Leaves of corn (C_4) had lower PEP carboxylase activity at the two higher UV dosages as compared with the "no UV" control. Some stimulation of PEP carboxylase activity, however, was noted in corn at the lowest UV-B dosage, equivalent to 6 percent ozone reduction. The reduction of PEP carboxylase activity at the two higher UV dosages, however, was quite pronounced. So, it may be concluded that the principal carboxylating enzymes in both photosynthetic models are, in the main, inhibited by UV or reduced in concentration in these four important crop plants.

The effects of visible light during UV-B irradiation of soybeans resulted in greater depression of photosynthesis by UV-B irradiation. However, if the visible radiation at high PPFD was given as a pretreatment, the results were thicker leaves, higher ratios of chlorophyll *a* to chlorophyll *b*, more UV-absorbing pigments, and reduced sensitivity in regard to photosynthesis by subsequent UV-B irradiance (Warner and Caldwell 1983). Warner and Caldwell conclude that this effect is indirect due to changes in morphological and physiological properties of the leaves, and not a direct concomitant and mitigating or repair process during UV-B irradiation. In a similar study, Mirecki and Teramura (1984) concluded that high levels of visible radiation ameliorated UV-B-induced injury in plants both by morphological changes and biochemical changes.

Photosynthesis rates under UV-B irradiation have been measured in at least one weedy or adventive species, Oenothera stricta (Robberecht and Caldwell 1983). This species is indigenous to the temperate latitudes of southern South America. However, it is adventive in the high equatorial Andes and also in the high mountains of Hawaii where UV-B radiation is unusually high (Caldwell et al. 1980). Photosynthetic rates of leaves exposed in growth chambers to UV-B radiation were not significantly reduced at dose rates representative of the radiation flux occurring in the habitats of this species. However, there was a significant photosynthetic depression observed at dose rates that exceed the field UV-B flux. The epidermis of the leaves of this species is a highly selective radiation filter that can attenuate up to 95 percent of the incident UV-B radiation and yet transmit between 70 percent and 80 percent of the visible radiation. Exposure to UV-B radiation significantly reduced the degree of epidermal UV-B transmittance by as much as 33 percent. The UV irradiation did not reduce the transmittance of visible light. This plasticity in regard to UV-B results from production of flavonoids and related phenolic compounds in the epidermis. This appears to be a good example of the ability of some kinds of plants to acclimate or adjust to some levels of UV-B irradiance.

EFFECTS OF UV-B RADIATION ON FLOWERS, POLLINATION, AND PRODUCTION OF SEEDS

Relatively little is known of the possible effects of UV irradiation on flowering, pollination, and seed production in plants. There has been some very recent work on the ultraviolet environment of pollen within unopened and opened flowers (Flint and Caldwell 1983a,b). Their experiments and measurements show that pollen grains in unopened flowers of most species are almost totally screened from solar ultraviolet-B radiation by the imbricated corollas in the unopened state. Also, the anther walls add to this protection from UV-B radiation. Once the pollen is freed, in vitro experiments showed that ultraviolet-B radiation typical of maximum levels occurring in middle latitudes did not significantly inhibit the germination of pollen grains. However, at UV-B levels characteristic of tropical mountains there was some inhibition of pollen germination. At this time, then, there appears to be little evidence that ultraviolet radiation, unless considerably increased, is detrimental to pollen and thus to the formation of seeds. However, because of the pioneer nature of the work so far and the number of processes between pollen formation and the production of viable seeds, it is premature to come to any definite conclusions in this regard. Clearly, more research is needed.

EFFECTS OF ULTRAVIOLET RADIATION ON COMPETITION AND INTERACTIONS WITHIN ECOSYSTEMS

Plants, either cultivated or wild, do not grow in isolation from other plants and animals. They must compete for space, light, nutrients, or water with other members of their species close by, or with populations of other species. Using wheat, wild oats, and goatgrass (*Aegilops*), Gold and Caldwell (1983) found that doses of UV-B can suppress competitive ability of some species in vegetational communities. Surprisingly, the weedy goatgrass was more repressed by UV-B than was wheat when the two were grown together. On the other hand, wild oats was more favored by UV-B than was wheat when the two were grown in 50:50 mixture in field plots with UV-B enhancement. Gold and Caldwell recommend long-term experiments on competitive interactions among populations in plant communities in the field under such enhanced UV-B irradiation. Based on his experience, Caldwell believes that significant changes in the competitive balance among species can be expected from changes in the solar UV radiation climate, and that this phenomenon may be more sensitive to changes in UV than effects on photosynthesis and alteration of monoculture yields.

One common and necessary interaction in most ecosystems, be it apple orchard or tropical rain forest, is the necessity of pollinating insects for production of fruits and seeds. Almost no information on the effects of UV-B irradiance on any common pollinating insect, even the honeybee, seems to be available.

SOLAR UV-B RADIATION AND EVOLUTION

Certainly throughout long, or even short, periods of time, solar ultraviolet radiation must be having effects on natural selection and evolution of plants and animals. The differences found in the photosynthetic rates of arctic and alpine ecotypes of *Oxyria digyna* when subjected to different levels of UV-B are an indication that, even within a single species, local populations have evolved tolerance or intolerance to UV-B in regard to this basic process (Caldwell et al. 1982). Caldwell and his co-workers found the same response in what are distinct but closely related species of dandelions (*Taraxacum*) and lupines (*Lupinus*) in arctic and tropical high-mountain environments that differ greatly in UV-B radiation flux densities.

Lee and Lowry (1980), in an imaginative paper, suggest that UV-B may be important as a possible factor in the upward migration and evolution of plant taxa. This hypothesis certainly is amenable to experiment. Two possible plant species might be examined in this regard: the arctic-alpine *Oxyria digyna* (Billings et al. 1971) and the weedy Andean *Oenothera stricta* (Robberecht and Caldwell 1983).

It also has been suggested that crop species originating in the tropics could be more resistant to UV-B than those originating in the temperate zone (Teramura and Caldwell 1983). This is a much more complex problem, since the basic field measurements would have to be made. There are also very likely to be a number of exceptions to the general hypothesis. Since so many of the crop species came into existence thousands of years ago, one should know the history of the UV-B climate in each region through time, certainly not an easy task.

RESEARCH RECOMMENDATIONS

Whether or not changes in stratospheric ozone proceed at a fast or slow pace, such changes would lead to some changes in UV-B radiation at the surface of the Earth and shifts in the latitudinal and elevational gradients of such radiation. Even if changes in stratospheric ozone are relatively small, spatial gradients in total ozone and UV-B exist now and have the possibility of limiting crop production in the lower latitudes. This seems important enough to continue research in progress on seed plants and UV-B and to start new research now on some of the points that are already obvious. The following list concerns some of the more urgent approaches.

- Since most of the work so far has been done in controlled and simulated environments, it is absolutely necessary to increase the small amount of experimentation being done under actual field conditions. This is where the real-life effects will be found; it will not be easy. Phytotron studies suggest the kinds of effects to expect in crop plants in the field even though such studies cannot be exactly extrapolated to field conditions. Growth-chamber studies are valuable guides to what needs to be done quantitatively in the field. In particular, more work is needed on action spectra in natural situations.
- Field studies should be initiated on the effects of UV-B on the competitive balance between plant populations. Crop plants and weeds are the most important in this regard. Such interactions may be quite sensitive to even small changes in UV climate.
- The inhibition of photosynthesis by UV-B irradiance is startling. Progress is being made in understanding this phenomenon at the whole plant level and at the biochemical level, but more work is needed. Such research should be encouraged, particularly to elicit the action spectra and dose responses.
- There appears to be some indication of an ability of plants to acclimate physiologically to different UV-B doses. This needs to be investigated as do possible effects on flowering and seed production.
- Since insect pollination is so important to fruit and seed production, there is a great need for some knowledge about the effects, if any, of UV-B on injury or mortality in pollinating insects such as bees.
- We need to know more about the synergisms at the biological level between UV-B and other stress factors such as drought, high temperatures, plant diseases, predatory insects such as the Japanese beetle, gypsy moth, and many others that eat plant parts. Also, what are the possible interactions between stratospheric ozone, UV-B and the current increases in atmospheric concentrations of carbon dioxide, methane, NO_x, and sulfur dioxide in relation to plant growth?
- What is the effect of UV-B irradiance as a selective force in evolution? This question is amenable to fairly straightforward experimentation. Such selection and evolution may be more rapid than is generally thought.

14

Effects of UV-B Radiation on Marine Organisms

INTRODUCTION

Because of the enormity of the ocean and the physical/chemical characteristics of the fluid we call seawater, the oceans are a major candidate for receiving large amounts of solar radiation. Therefore, we might expect that the photochemical and photobiological effects resulting from radiating ocean waters would be well understood. They are not.

This is not to say that oceanographers and marine biologists have let the effects of UV light go unnoticed. The importance of UV light had been considered by earlier practitioners in the attempt to measure primary productivity. Moreover, marine biologists observing the vertical distribution of invertebrates and fishes quickly noticed differences in pigmentation of organisms in surface layers as opposed to those in deep water. They attributed these differences to "solarization," and speculated on the impact of UV in forcing a protective coloration.

We are virtually at the beginning of understanding the effects of short wavelengths of light on organisms and biochemical processes in the sea. Much of the impetus for research on this topic has come from concerns about potential changes in stratospheric ozone resulting from human activities. Only within the last decade has this subject been addressed, and almost all of the research that has been conducted has been supported by the U.S. Environmental Protection Agency (EPA).

The strategy and structure of the research program sponsored by EPA can be characterized as one that features a "trophic approach." This approach selects representatives from various trophic levels for experimental testing. In abbreviated terminology, the members of the trophic structure are the primary producers (photosynthetic algae), primary herbivores (zooplankton and their larvae), and fish larvae that inhabit the surface waters of the oceans. In addition, the EPA sponsored research concerning the factors affecting the penetration of UV light in the sea and the modeling of the effects that UV light would have on organisms residing in the upper layers.

In cooperation with the North Atlantic Treaty Organization (NATO), EPA sponsored a symposium, held in Copenhagen, Denmark, on the effects of UV light in the marine environment. This resulted in a publication that featured, for the most part, reviews of current knowledge on the effects of UV radiation in the marine environment (Calkins 1982). We summarize the important aspects of papers presented in that volume. (The reader should consult Calkins for the original references.)

PENETRATION OF UV RADIATION IN THE OCEAN

The amount of UV light received at the sea surface is a function of latitude, the transparency of the atmosphere, and the characteristics of the sea surface. Thus, in attempting to make an estimate for any one area of the amounts of radiation received at the sea surface, one must take into account these features--as well as the thickness of the ozone layer. At the moment this type of estimate for a specific area is very difficult to make. However, in a general sense it is reasonable to assume that the lower latitudes, that is, tropics with clear seawater, are the areas receiving the greatest amounts of solar UV.

Once UV radiation has penetrated the ocean surface, the individual wavelengths are subject to scattering and absorption by molecular and particulate matter in the water, but very little is backscattered out of the water. The ultimate fate of these wavelengths is to be absorbed by dissolved colored pigments, colored particulate substances such as phytoplankton algae, and other nonbiogenetic substances capable of UV absorption (Figure 14-1). The amounts of these absorbing substances are highly variable, and it is very difficult to generalize about the effectiveness of UV penetration for any one given area of the ocean based on their spatial distribution. We can say, speaking very generally, that UV-absorbing,

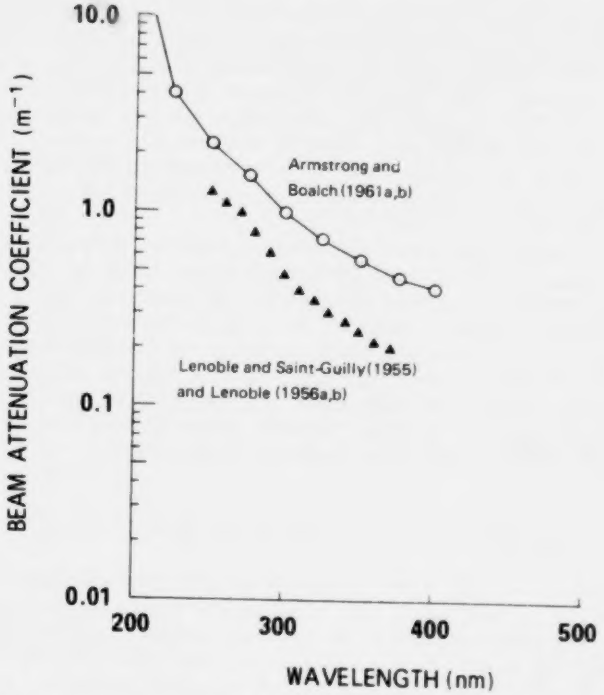

FIGURE 14-1 Beam attenuation coefficient of artificial seawater as a function of wavelength. SOURCE: Adapted from Smith and Tyler (1976).

dissolved yellow material enters the ocean primarily by way of fresh water. Hence, the concentrations of these substances is highest in most coastal regions of the world (Jerlov 1976, Hojerslev 1982). Also, primary productivity--and hence the abundance of phytoplankton--occurs in the coastal regions of the oceans. Therefore, as a general rule of thumb, the UV wavelengths penetrate deepest in the clear, deep ocean waters of lower productivity and are attenuated more effectively in turbid coastal waters of higher productivity.

The dissolved yellow substances that absorb UV radiation are complexes of organic compounds that are largely of plant origin. Discharges of these substances from large river systems, such as the Amazon, cover large areas of the ocean and can be seen many miles at sea from their origin. Phytoplankton and algae and attached floating seaweed are also sources of yellow material, but in comparison with the freshwater input, these are minor. The fate of these yellow, UV-absorbing compounds after they are once discharged in the ocean is not well understood, but there is some indication that this dissolved material is absorbed onto particulate matter that eventually settles out of the water column reaching the bottom floor. Photooxidation and enzymatic bacterial decomposition are also distinct possibilities. The "protective action" by the presence of dissolved yellow pigments has yet to be demonstrated. The hypothesized protection is based wholly on their characteristics of short-wavelength absorption and their abundance and persistence in the coastal waters of the ocean.

EFFECTS ON PHYTOPLANKTON AND PRIMARY PRODUCTION

Some of the early research on photosynthetic processes featured the effects of UV. These interests carried over into the field of measuring primary productivity of the oceans, that is, the measurement of photosynthetic carbon fixation by marine phytoplankton. The early measurements compared carbon fixation rates in glass and quartz bottles. More recent experimentation has focused on supplementing solar radiation with artificial UV-B. All studies have shown that the short wavelengths of solar radiation inhibit photosynthesis, and in general are responsible for photoinhibition by high light intensities (Worrest et al. 1980).

Experiments show that the effects of UV light can occur to an average depth of about 5 m in coastal waters and in clear water to approximately 30 m. The effect on photosynthetic carbon fixation is highest in the surface waters, where as much as 50 percent reduction of carbon fixation can occur compared with the controls. However, when the UV effects are integrated over the entire water column there is only approximately 2 percent reduction in carbon fixation by UV inhibition.

Most of the research has shown that UV affects carbon fixation in a matter of minutes, and that phytoplankton taken from depths where light intensities are low (those organisms residing at the base of the euphotic zone) are much more sensitive to the UV effects than are organisms from the surface.

The problem in making these estimates from experiments with augmented UV-B radiation arises because of the distribution of organisms in the water column and mixing in the surface layers. To estimate mixing is a difficult physical problem. For example, the energy for mixing comes from tides or wind, which complicates the prediction. What can be said is that the effects of vertical mixing will greatly influence the average amount of UV radiation that a single cell receives. Mixing reduces the total amount of UV light reaching the cell. Aquarium studies cannot practically take account of these types of influences on effects of UV-B on organisms in their natural habitats.

With studies in photosynthesis, many workers have shown changes in chlorophyll content as a function of depth as well as diurnal changes in chlorophyll content. These are suspected to be due to effects of change in amounts of short-wavelength radiation (Worrest 1982).

The action spectra for UV-B effects appears to be a mixture of the monochromatic action spectra for photosynthesis and that for DNA (Smith et al. 1980). For those species that have been tested in the laboratory, photosynthetic rate falls rapidly as a function of wavelength, coincident with a decline in the absorbing capacity of the photosynthetic pigment system at shorter wavelengths. Below 300 nm the photosynthetic rate is low. Prolonged exposure to UV-B and/or UV-A wavelengths gives rise to rapid photoinhibition of oxygen evolution and photooxidation.

Because of the high species diversity of natural populations, research has compared the effects of ultraviolet light on photosynthetic rate, growth, biomass, and pigment content. These studies have shown that some species are more sensitive than others to UV-B, and the difference appears to be due to either presence of pigment protective screens or cellular reflective mechanisms and/or "protective sequences" due to DNA organization (Yentsch and Yentsch 1982).

It is speculated that the largest problem for primary producers exposed to increased UV-B might be changes in the species diversity of phytoplankton communities. It is argued that due to the difference in sensitivity of species, a general transition from eukaryotes to procaryotes could alter the quality and perhaps the quantity of organic production, and this in turn could affect the characterization of food stocks and the character of trophic levels of the marine food web.

Marine microbiologists have long noted that the bacteria in the surface waters of the oceans are highly pigmented, and most of these pigments appear to be caratenoids. In laboratory experiments in which marine bacteria were exposed to visible radiation supplemented with UV, increases in total numbers of pigmented cells and decreases in the number of organisms capable of growing on cellulose were recorded (Worrest 1982). In all species tested there is an overall increase in bacterial respiration. Researchers agree that bacterial plankton assemblages are altered by UV-B radiation; however, there is some indication that the alterations might be secondary effects associated with interactions between other trophic levels that supply bacterial substrate.

EFFECTS ON INVERTEBRATES

Some of the very early literature on the effects of ultraviolet concerns the rearing of larval invertebrates in light and darkness. In all cases reported, full sunlight appears to be detrimental: fewer organisms survived in strong sunlight than in darkness. Using dominant copepod species of plankton communities, experimenters have compared the effects of sunlight with and without ultraviolet components, and shown that the UV component stresses the general physiology of these organisms (Damkaer et al. 1980).

Animals that live in the upper layers of the ocean appear to be more resistant to UV stresses than those living at depth. To date, the effects of UV-B on copepods, euphausids, and the planktonic larvae of shrimp and crabs have been studied using augmented UV-B. In the copepods tested, the effects of ultraviolet light appear to increase mortality of the adult and the survival of the early stages of larvae and to decrease the fecundity of the survivors. Male adults appear to be more sensitive than females, and the young larval stages are more sensitive than the old. There also appears to be a long-term effect caused by UV light on the capability of larvae to survive. This effect is transferred by the parents to the larvae: experiments have shown that the numbers of eggs and larvae produced are reduced significantly by the parents exposed to UV-B, and the capability of survival of these eggs and larvae is reduced significantly if they are produced by parents exposed to UV-B.

Investigation of biological effects of UV-B on marine plankton have included a variety of approaches ranging from histological sectioning to simple survival studies. Most of the modern work has been concerned with the direct effect of natural or enhanced UV-B on the survival of marine zooplankton. The assumption implicit to the conclusions of this work is that the organisms that live in the near surface layer will be exposed to ambient UV-B radiation regardless of its intensity. Most of these workers feel that the organisms are living near their UV tolerance limits, and in the course of time have evolved mechanisms to protect against natural fluctuations in UV-B radiation. In addition to the assumption of photorepair, these workers point out that phytoplankton possess the ability to avoid harmful levels of UV-B by "defensive behaviors." Implicit in that assumption is that the organisms can "sense" UV-B and avoid it by swimming or sinking below the surface. This suggests that the swimming mechanism would be tied to vertical migration, which would presumably be the result of the organisms' detection of changes in the amount of ambient light as sensed through visual pigmentation. The eyes of many planktonic crustaceans contain carotenoid pigments that have the capability of absorption in the near UV-B. As yet there is no evidence that photoreactivation or repair occurs in these organisms.

A number of workers have called attention to the protective action of blue UV-absorbing pigments that occur in a number of organisms that reside in the surface waters of the oceans (Worrest 1982). These pigments are found in planktonic crustaceans, such as copepods and marine insects.

Many of the motile benthic invertebrates avoid bright sunlight by burrowing or moving into deeper water. Among the attached species, it has been observed that UV radiation causes retraction of tentacles of sea anemones. For example, so called shade-loving sponges and tunicates die in one or two days when exposed to UV solar radiation. Some similar species are capable of being resistant to UV by heavy protective coloration.

EFFECTS ON FISH LARVAE

Most of the early data on the impact of UV radiation in fish came from hatchery studies. Also, a number of researchers have pointed out that solar UV radiation can be stressful to fish eggs which float at the surface. These experiments demonstrate that the effects of UV radiation increase the mortality of eggs. For example, laboratory tests, which modify the solar spectrum to fit the DNA action spectrum, have shown that UV-B radiation will markedly reduce the survival of larval anchovy (Hunter et al. 1979). Cytological and morphological studies have shown that UV exposure results in damage to both the brain and the eye of the anchovies. Similar tests have produced lesions in mackerel larvae. The effects appear to be manifested through the pigments in these larvae (Hunter et al. 1979).

Researchers believe that three factors--seasonality for spawning, the vertical distribution, and photorepair mechanisms--could offset the effects that would be caused by changes in the ozone layer. The research on anchovy larvae has shown that the effects of UV are seasonal. The larvae suffer significantly more mortality from February to October than at other periods. The sensitivity of anchovy to UV light depends on its stage of development. The eggs are least sensitive to UV radiation. Yolk sac larvae are twice as sensitive as eggs. Swimming larvae apparently can avoid potential UV stress by vertical migration. The seasonality, coupled with other environmental factors, tends to minimize the UV effect.

Experiments have demonstrated that photorepair processes are sufficient to repair all of the UV-B damage in laboratory work on anchovy. The repair influence needed to stimulate complete repair was about 10 percent of that available from the sun during a clear day at 33°N. Estimates of the amount of photorepair influence entering the sea surface indicate that photorepair in anchovettes would operate maximally at any depth even under the added stress of increased UV-B due to ozone depletion.

One of the principal reasons that one might minimize the relative effects of increased UV-B radiation from even a large (of order 25 percent) decrease in ozone is the fact that anchovy larvae are abundant at depths well below the upper few meters. The estimates of increased UV-B with even a 25 percent reduction in ozone indicates that there would be approximately a 1-m increase in the depth of penetration of short-wavelength radiation. It can be argued that this would not have a major effect on the population of anchovy larvae, which is distributed over 60 m.

RESEARCH RECOMMENDATIONS

The objectives of research on the effects of UV radiation on marine organisms have been and continue to be to access the role of change in characteristics of short-wavelength radiation as a potential factor in biochemical evolution of ocean ecosystems. Most researchers believe that surface-living marine organisms are currently at the upper level of tolerance to UV radiation. The research community should be encouraged

- to perform comparative studies of organisms currently known to cope with high intensities of UV, and
- to elucidate the mechanisms of survival.

It is anticipated that such studies will provide insight into the mechanisms that have favored evolutionary development in different habitats of the world's oceans.

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Appendix:

Biographical Sketches of Committee Members

LEONARD C. HARBER is Chairman of the Department of Dermatology at Columbia University's College of Physicians & Surgeons and Director of the Dermatology Service at Columbia-Presbyterian Medical Center in New York City. He received his education at Johns Hopkins University (A.B.), New York University (M.D., M.S.), and has been a guest investigator at the Rockefeller University and Fulbright Research Scholar at the University of Copenhagen. His major research interests are in photobiology and photochemistry. His primary research efforts are concerned with the pathologic effects of sun and artificial light sources on the skin.

DANIEL L. ALBRITTON is the leader of the Atmospheric Sampling Group of the Aeronomy Laboratory of the National Oceanic and Atmospheric Administration in Boulder, Colorado. He received his Ph.D. in physics from the Georgia Institute of Technology in 1967. He is Chairman of the Natural Sources Task Group of the Interagency Task Force for acid precipitation research. He also serves on the executive committee of the Global Tropospheric Experiment of the National Aeronautics and Space Administration. His research interests are in atmospheric chemistry, particularly the field measurement of trace constituents.

WILLIAM DWIGHT BILLINGS is James B. Duke Professor of Botany at Duke University where he received his Ph.D. degree. His research interests are concerned with the ecology of plants and ecosystems in regions of climatic stress: the Arctic, the high mountains of western North America, South America, and New Zealand, and North American deserts. At present, his research is primarily concerned with the effects of increasing

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CO_2 and climatic changes on ecosystems of these regions. He is a Past-President of the Ecological Society of America and a Fellow of the American Academy of Arts and Sciences.

CHARLES R. CANTOR has been Chairman of the Department of Human Genetics and Development at Columbia University since 1981. He received his Ph.D. in chemistry from the University of California, Berkeley, in 1966. From then until 1981 he was a faculty member in Columbia's Chemistry Department. His major research interests are the molecular biology and biophysical chemistry of nucleic acids. He has been particularly involved in using photochemical and photophysical techniques to study complex nucleoprotein assemblies such as viruses, chromosomes, and ribosomes.

JULIUS S. CHANG is Director of the Acid Deposition Modeling Project at the National Center for Atmospheric Research (NCAR). He joined the Lawrence Livermore National Laboratory in 1966 and was the Deputy Division Leader for Theoretical Physics prior to joining NCAR in 1983. He received his Ph.D. in applied mathematics and statistics from the State University of New York at Stony Brook in 1971. His research interests are computational physics, mathematical modeling of chemical processes in the atmosphere, and, in particular, the chemistry of stratospheric ozone.

PAUL DONALD FORBES is an Associate Professor in Dermatology, and Associate Director of the Center for Photobiology, at the Temple University Health Sciences Center, Philadelphia. He received his Ph.D. in biology from Brown University in 1961. His research interests are in cutaneous photobiology and radiobiology.

JAMES R. HOLTON is a Professor of Atmospheric Sciences at the University of Washington, and a Senior Fellow in the Joint Institute for the Study of the Atmosphere and the Oceans, University of Washington. He received his Ph.D. in meteorology from M.I.T. in 1964. His primary research interests are in large-scale dynamical processes in the troposphere and stratosphere.

FREDERICK KAUFMAN is University Professor of Chemistry and Director of the Space Research Coordination Center at the University of Pittsburgh. He received his Ph.D. in chemistry from the Johns Hopkins University in 1948. He was elected to membership in the National

Academy of Sciences in 1980. His research interests are in the fields of gas phase kinetics of elementary reactions and of energy transfer, including their application to upper atmosphere science, combustion, and chemical lasers.

ALFRED W. KOPF, M.D., is a Clinical Professor in the Department of Dermatology at New York University School of Medicine. His major research interest has been in the field of cutaneous oncology with emphasis on malignant melanoma. His more recent work concerns the identification of prognostic factors that predict the outcome of human malignant melanomas. This work utilizes a large computerized data base of over 1,000 patients who have been afflicted by this cutaneous neoplasm.

MARGARET L. KRIPKE has recently assumed the chairmanship of the Department of Immunology at the University of Texas M.D. Anderson Hospital and Tumor Institute in Houston, Texas, and holds the Kathryn O'Connor Research Professorship at this institution. Previously she was a Laboratory Director at the National Cancer Institute's Frederick Cancer Research Facility in Frederick, Maryland. She received her Ph.D. degree in immunology in 1970 from the University of California at Berkeley and since then has carried out research on the role of the immune system in carcinogenesis. Her work in an experimental photocarcinogenesis system led to the discovery that exposure to UV radiation produced systemic immunological changes.

ANGELO A. LAMOLA has been a member of technical staff at AT&T Bell Laboratories since 1966 and presently serves as Head, Molecular Biophysics Research Department. His research interests have included organic photochemistry and photobiology, including the ultraviolet-light-induced alterations of DNA.

MICHAEL J. PRATHER is Research Associate in the Division of Applied Sciences at Harvard University. He received his Ph.D. degree in astronomy at Yale University in 1976. His research interests focus on the physical and chemical processes in earth and planetary atmospheres. He and his colleagues at Harvard, Jennifer Logan, Steven Wofsy, and Michael McElroy, are responsible for the stratospheric model used for some of the calculations cited in this report.

ROBERT S. STERN is Assistant Professor of Dermatology at Harvard Medical School and dermatologist at the Beth Israel Hospital in Boston. He received an A.B. in economics in 1966 from Harvard College and an M.D. in 1970 from the Yale University School of Medicine. He has done clinical work and research in photomedicine. He is particularly interested in the joint application of epidemiologic methods and cost-effectiveness analysis to determine the relative risks and benefits of various treatments for skin disease with utilization of UV radiation. He directs the Photochemotherapy Follow-up Study, is a member of the Institute for Health Research at Harvard, and is associate editor of the *Archives of Dermatology*.

RICHARD P. TURCO is a Senior Research Scientist at R&D Associates, Los Angeles, California. He received his Ph.D. in electrical engineering and physics from the University of Illinois in 1971. Dr. Turco's major research interests include atmospheric photochemistry and chemical cycles, aerosol processes and properties, planetary atmospheres and clouds, and effects of atmospheric composition on climate. He is a member of the Scientific Committee on Problems of the Environment investigating the global atmospheric and ecological impacts of nuclear warfare under sponsorship of the International Commission of Scientific Unions.

CHARLES S. YENTSCH is Director of the Bigelow Laboratory for Ocean Sciences in West Boothbay Harbor, Maine. He holds an M.S. degree from Florida State University (1953) and engaged in further graduate studies at the University of Washington, Seattle. His recent research interests include the nature of light in the sea and its interactions with marine organisms.